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**ADB011769**

# **SYNTHESIS AND MODIFICATION OF CARBOXYLATED POLYPHENYLENES AND PHENYLATED POLYIMIDES**

**WRIGHT STATE UNIVERSITY  
DAYTON, OHIO 45431**

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**TECHNICAL REPORT AFML-TR-76-9  
FINAL REPORT FOR PERIOD 1 NOVEMBER - 15 NOVEMBER 1975**

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Carboxylated and phenylated biscyclopentadienones have been copolymerized with aromatic dialkynes to afford a series of carboxylated phenylated-polyphen- ylenes. The polyphenylenes were converted to the corresponding potassium, magnesium, and barium salts to afford a series of aromatic ionomers. All but one of the potassium ionomers are soluble in dimethylsulfoxide and can be cast into thin films that tough, flexible, water white, and transparent. The magnesium and barium ionomers are insoluble in common organic solvents. Thermo- gravimetric analyses of the barium ionomer show no weight loss until near 500°C.			

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A phenylated biscyclopentadienone containing a pyridine linkage has also been prepared and polymerized with *p*-diethynylbenzene. The resulting polypyridine is soluble in chloroform and reacts with hydrogen chloride to form the corresponding hydrochloride. Several phenylated polyimides have been prepared by the polymerization of phenylated dianhydrides with aromatic diamines. The polyimides are soluble in chloroform and can be cast into thin films that are flexible, slightly yellow, and transparent. The thermally-stable polymers show glass transition temperatures as low as 238°C. An ethynyl-substituted diamine was prepared and polymerized to afford a phenylated polyimide with pendent ethynyl substituents. This polymer undergoes thermal crosslinking near 250°C to yield a thermally-stable material that is completely insoluble. Finally, acetylene-terminated polyphenylene oligomers were prepared from a biscyclopentadienone and excess *p*-diethynylbenzene. These oligomers undergo thermal crosslinking near 250°C without the evolution of volatiles to afford insoluble, thermally-stable resins.

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## FOREWORD

This report was prepared at Wright State University, Dayton, Ohio 45431, under AF Contract No. F33615-75-5073. The Contract was initiated under Project No. 7342, "Nonmetallic and Composite Materials", Task No. 734201, direction of the Air Force Materials Laboratory, Dr. F.E. Arnold, (AFML/LNP), Project Engineer.

This report covers work conducted from 1 November 1974 to 15 November 1975. It was released by the authors December 1975.

This technical report has been reviewed and is approved for publication.

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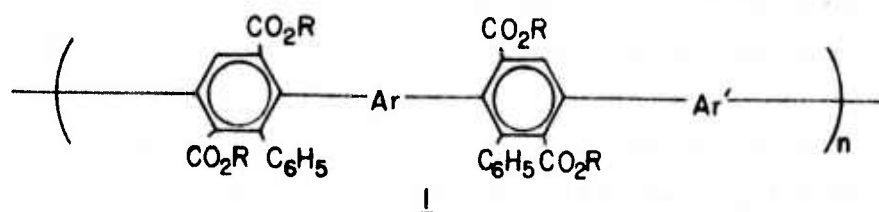
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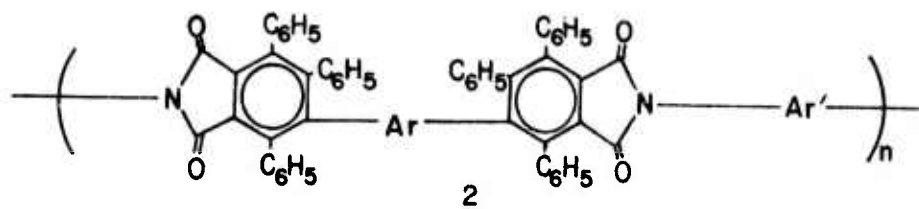
## SECTION I INTRODUCTION

A series of high-molecular-weight, carboxylated polyphenylenes (1) had been prepared in this laboratory by the Diels-Alder reaction of bis-cyclopentadienones with *p*-diethynylbenzene.<sup>1</sup> The polyphenylenes were soluble in chlorinated-hydrocarbon solvents and could be cast into films



that were flexible, tough, colorless, and transparent. The polymers decarboxylated at 360-380°C in a nitrogen atmosphere to form crosslinked systems that were insoluble.

A series of phenylated polyimides (2) had also been prepared in this laboratory by the polymerization of phenylated dianhydrides with aromatic diamines.<sup>2</sup> These polymers were soluble in chlorinated-hydrocarbon solvents and had intrinsic viscosities as high as 4.1. The polyimides could



be cast into films that were flexible, tough, slightly yellow, and transparent. Thermal gravimetric analyses of these polymers in air and nitrogen atmospheres showed no weight loss until near 530°C. The polyimides' glass transition temperatures ranged from 360 to 471°C.

The major goal of this research was the modification of the carboxylated polyphenylenes and phenylated polyimides so as to provide materials with applications of special interest to the U. S. Air Force. For example,



it was postulated that the formation of the Group I and Group II metal salts of the carboxylated polyphenylenes would afford materials with excellent optical properties, high impact strengths, and high abrasion resistances.<sup>3</sup> These properties combined with their thermal stability were expected to make the "aromatic ionomers" suitable for use in windshields and canopies on supersonic aircraft.<sup>4</sup> Another planned structural modification was the introduction of heterocyclic rings into the polymer backbone. The increased polarity was expected to enhance the polymers' adhesion to fibers and metals.

The phenylated polyimides were to be modified so as to provide thermally-stable laminating resins that could be crosslinked without the evolution of volatile materials. The crosslinking mechanism selected involved the thermal polymerization of pendent ethynyl groups. Hence, a project was initiated to incorporate ethynyl groups along the polyimide backbone. A project aimed at lowering the phenylated polyimide glass transition temperature below 250°C, the temperature at which thermal crosslinking was expected to occur,<sup>5,6</sup> was also initiated. This was to allow the polymers to be melt processed prior to crosslinking.

## SECTION II

### DISCUSSION

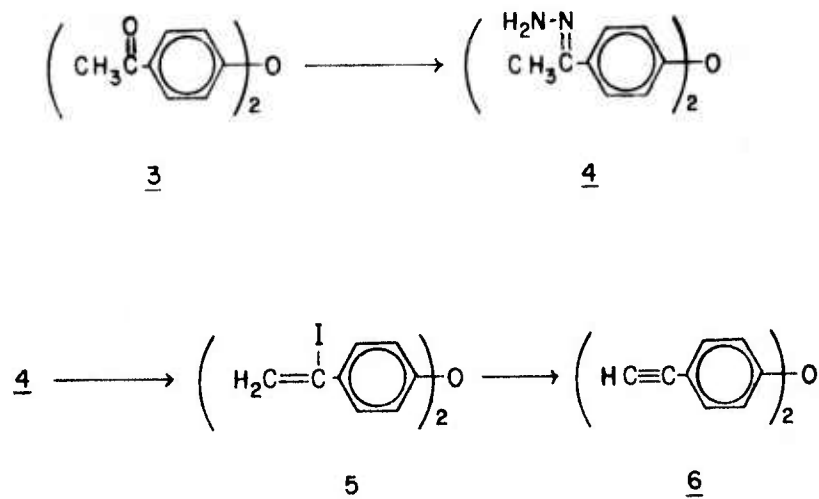
#### 1. Modification of Carboxylated Polyphenylenes

##### a. New monomers

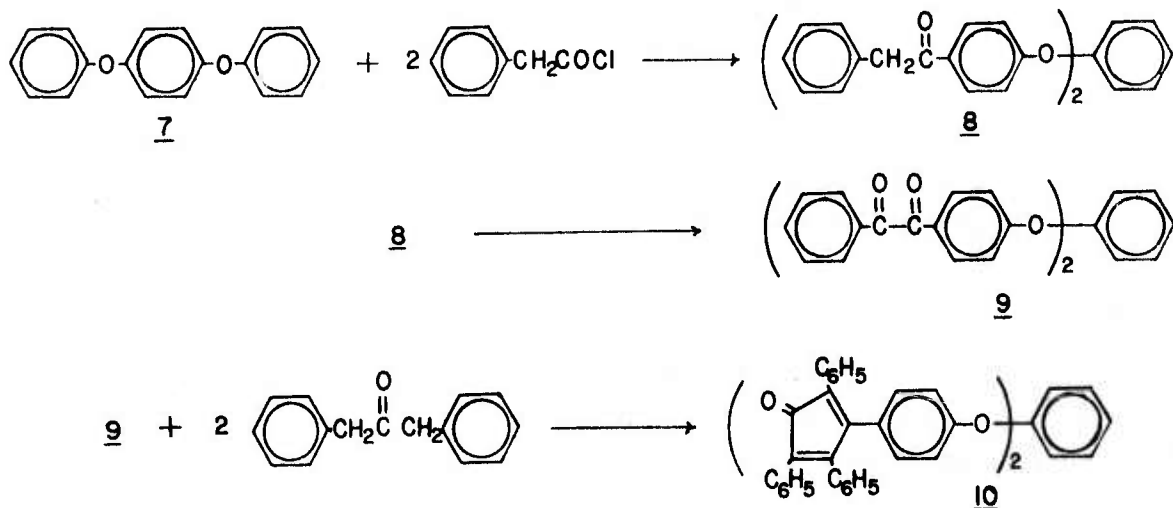
It was anticipated that the aromatic ionomers would display high transition temperatures making processing difficult. Therefore, several new monomers containing diphenyl ether linkages were synthesized. The incorporation of these flexible linkages in a polyphenylene backbone is known to lower the glass transition temperature.<sup>7</sup>

Our initial attempt to prepare 4,4'-diethynyldiphenyl ether (6)<sup>8</sup> from 4,4'-diacetyldiphenyl ether (3) via a DMF/POCl<sub>3</sub> complex<sup>9</sup> was unsuccessful. Hence, the following synthetic route was carried out.<sup>10</sup> The reaction of 3 with hydrazine gave a 70% yield of the hydrazone 4. Treatment of 4 with iodine afforded 4,4'-bis( $\alpha$ -iodoethenyl)diphenyl ether (5), which was dehydrohalogenated with base to give compound 6 in

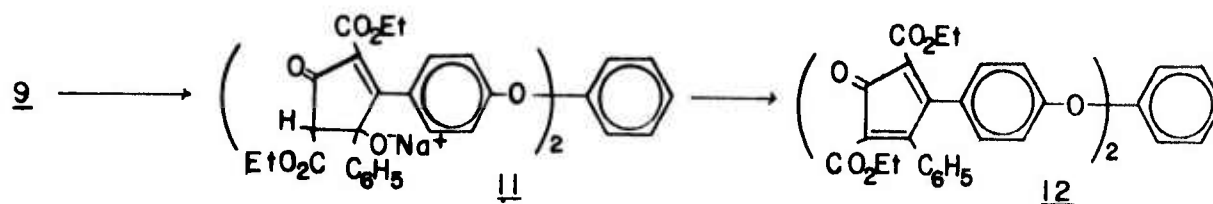
85% yield. The diethynyl monomer was sublimed immediately prior to use.



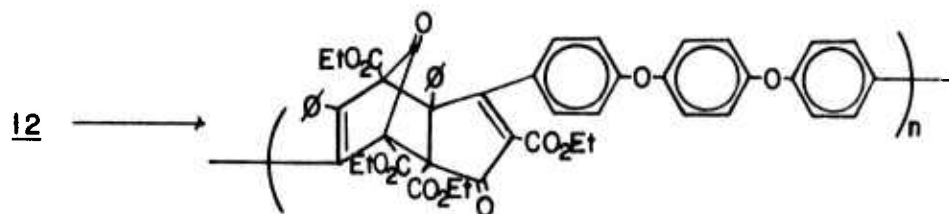
Two ether linkages were then incorporated in a biscyclopentadienone monomer. Treatment of 1,4-diphenoxybenzene (7) with phenylacetyl chloride gave the diketone 8. The diketone was oxidized with selenium dioxide to yield 1,4-bis(p-phenylglyoxalylphenoxy)benzene (9) which upon condensation with diphenylacetone afforded the dark-purple biscyclopentadienone 10. This monomer was purified by chromatography on alumina with toluene: ether.



Tetraketone 9 was also condensed with diethyl 1,3-acetonedicarboxylate to yield the biscyclopentadienone salt 11, which upon subsequent acidification and dehydration gave the biscyclopentadienone 12. The bright-orange monomer was purified by chromatography on silica gel with chloroform:ether. Compound 12, however, slowly changed from



bright orange to light yellow when stored in the solid state at ambient temperature. The color change was accompanied by the appearance of a new infrared absorption band at  $1770\text{ cm}^{-1}$ , characteristic of carbonyl-bridged compounds.<sup>11</sup> This indicates that the biscyclopentadienone is homopolymerizing via Diels-Alder dimerizations. The homopolymerization greatly limits the use of this monomer in polymerizations with dialkynes. Since, even if it were prepared immediately prior to use, the facile self-dimerization would compete with polymerization with the alkyne.

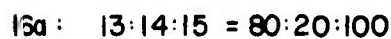
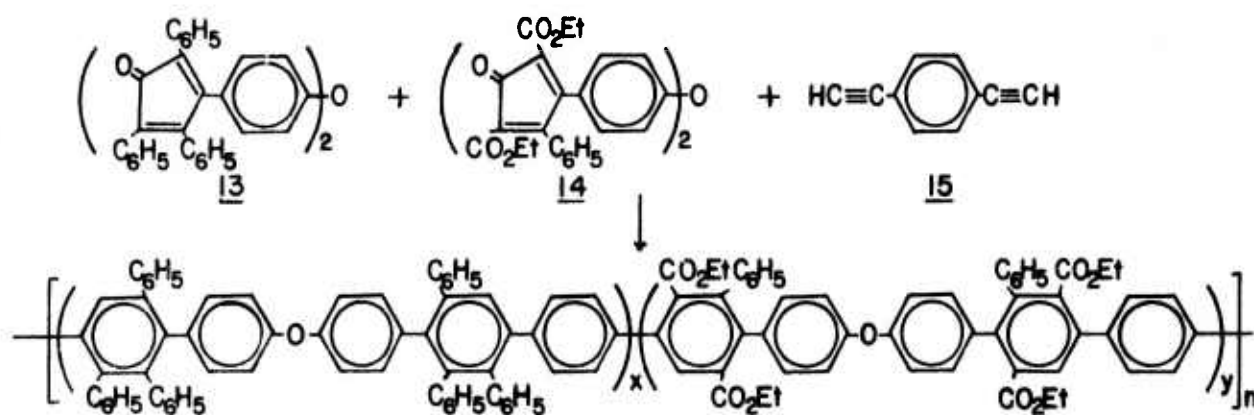


b. Copolymerization of carboxylated and phenylated biscyclopentadienones with aromatic dialkynes.

Since commercial ionomers exhibit their optimum physical properties at low crosslink densities, a project was carried out to reduce the number of crosslinking sites (carboxylic groups) along the polyphenylene backbone.<sup>12</sup> The approach employed involved the copolymerization of carboxylated and phenylated biscyclopentadienones with aromatic dialkynes.

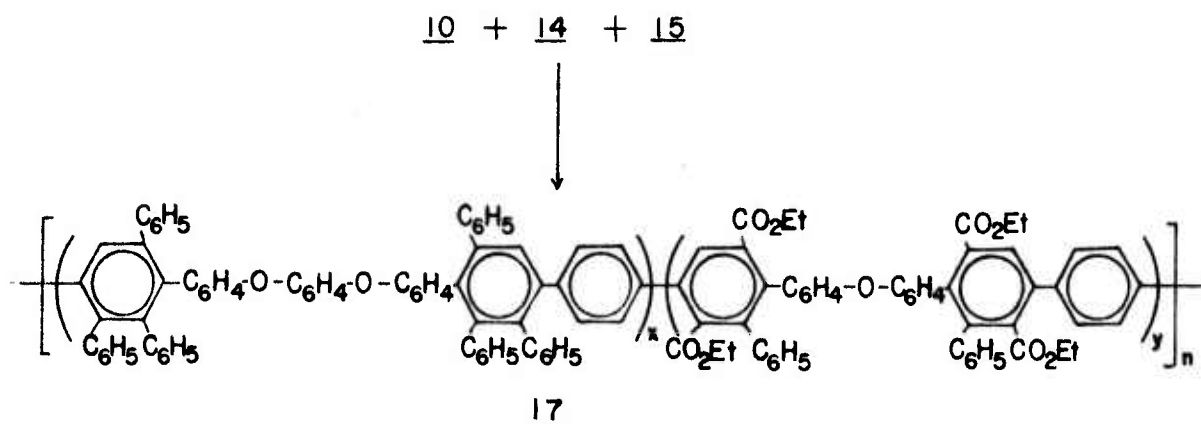
In this manner, phenylated polyphenylenes were prepared that contained low percentages of pendent alkoxy carbonyl substituents.

The biscyclopentadienones 13 and 14 were copolymerized with *p*-diethynylbenzene (15) in molar ratios of 80:20:100 and 95:5:100 to produce the polymers 16a and 16b, respectively (Table 1). The polymeri-



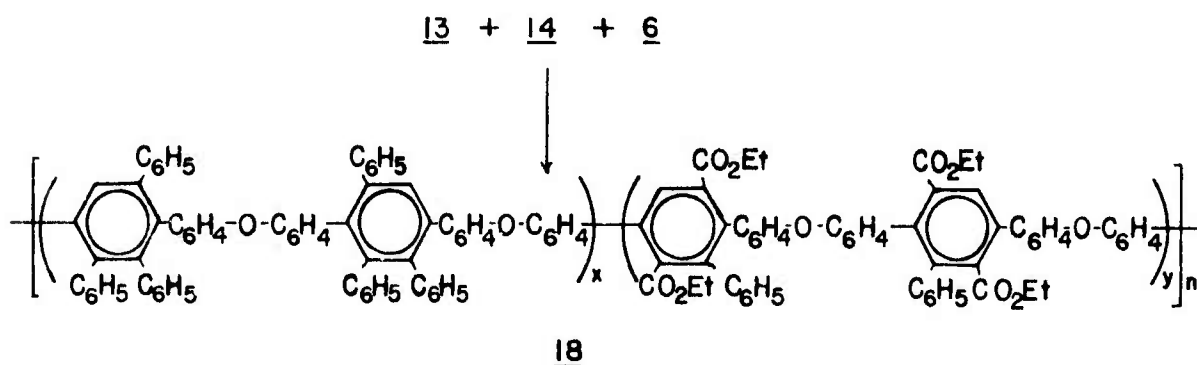
zations were carried out in chlorobenzene contained in sealed polymerization tubes. The tubes were heated at 110°C for 18 hr and then at 225°C for 48 hr. The polymers are soluble in chlorinated hydrocarbons and in aromatic solvents. Thin films can be cast from chloroform that show infrared absorptions characteristic of phenylated and carboxylated polyphenylenes (Figures 1 and 2). Thermogravimetric analyses of pellet samples in air and nitrogen atmospheres show initial weight losses between 365 and 550°C, which correspond closely to the calculated weight percentages of pendent ethoxycarbonyl groups (7.2 and 1.7%, respectively) in the copolymers (Figure 3). After the initial weight loss, the TGA curves closely resemble the TGA curves of phenylated polyphenylenes.

In a similar manner, the biscyclopentadienones 10 and 14 were copolymerized with 15 in a molar ratio of 80:20:100. Polymer 17 is soluble in chlorinated hydrocarbons and has an inherent viscosity of 1.05



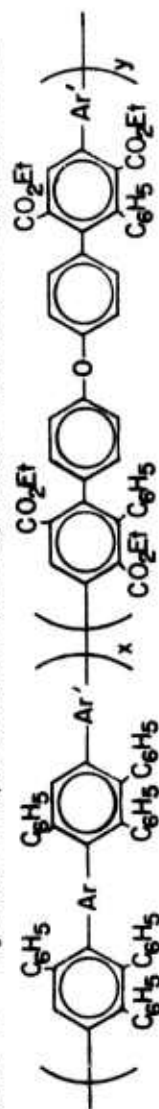
(Table 1). Thermogravimetric analyses show an initial 5-6% weight loss between 380 and 560°C in air and nitrogen atmospheres, which also corresponds closely to the calculated weight percentage of pendent ethoxycarbonyl groups (6.3%) in the copolymer (Figure 4).

Finally, polymer 18 was prepared by the copolymerization of the biscyclopentadienones 13 and 14 with 4,4'-diethynyldiphenyl ether (6). The molar ratio of 13:14:6 employed was 80:20:100.



Polymer 18 is soluble in chlorinated hydrocarbons and has a Tg of 247°C (Table 1). The polymer also loses an amount of weight (5-6%) between 380 and 560°C nearly equivalent to its calculated weight percentage (6.2%) of ethoxycarbonyl substituents (Figure 5).

Table 1. Physical Properties of Carboxylated Phenylated Polyphenylenes



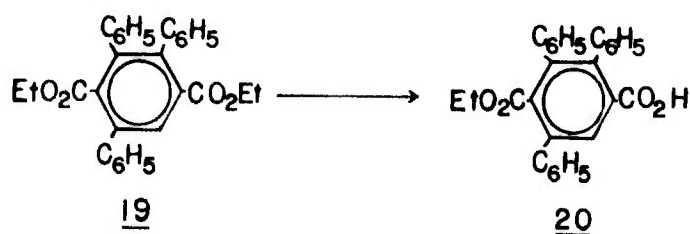
Polymer	Ar	Ar'	Mole Percent of Repeat Unit x y	$\eta_{inh}^a$	Tg <sup>b</sup>	Analyses <sup>c</sup> C H
16a			80 20	0.77	278	89.88 5.23 89.69 5.43
16b	"	"	95 5	0.49	—	92.16 5.21 91.55 5.23
17			80 20	1.05	261	88.95 5.16 88.44 5.37
18			80 20	0.77	257	88.74 5.15 88.56 5.30

<sup>a</sup>Inherent viscosities in sym-tetrachloroethane at 0.25 g/dl at 30°. <sup>b</sup>°C. <sup>c</sup>Calcd/Found.

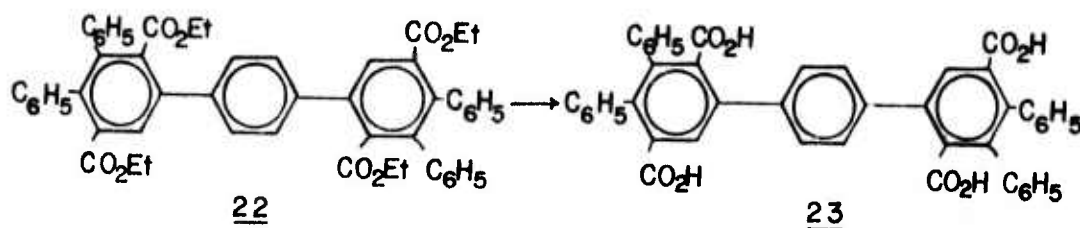
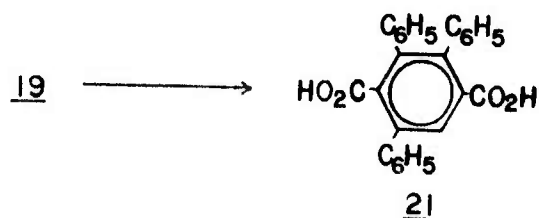


c. Hydrolysis of model compounds

A study of the hydrolysis of ethoxycarbonyl-substituted model compounds was carried out in order to determine the conditions necessary for the hydrolysis of the corresponding polymers. The hydrolysis of diethyl 2,3,5-triphenylterephthalate (19) in refluxing ethanol containing potassium hydroxide and in DMSO containing potassium t-butoxide<sup>13</sup>

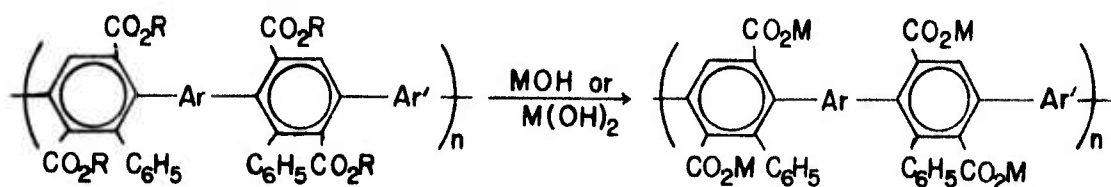


afforded the partially hydrolyzed ester 20. The model compound 19, however, was converted to 2,3,5-triphenylterephthalic acid (21) when the hydrolysis was carried out in refluxing ethylene glycol containing potassium hydroxide. Similarly, the hydrolysis of model compound 22 in refluxing ethylene glycol yielded the tetraacid 23. The hydrolyzed model compounds displayed infrared absorptions characteristic of organic acids (Figure 6).<sup>14</sup>

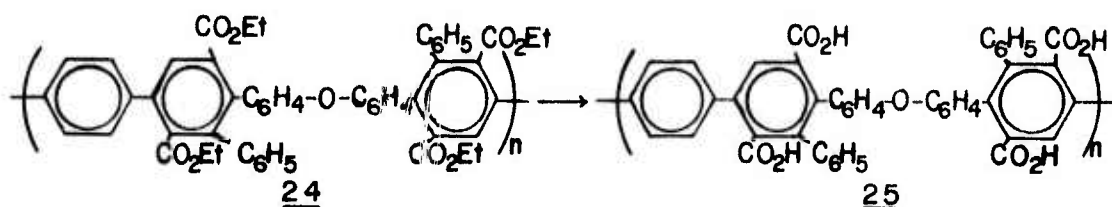


d. Formation of aromatic ionomers

A study aimed at the conversion of alkoxycarbonyl-substituted polyphenylenes to their Group I and Group II metal salts was then carried out. The polymers were hydrolyzed with the appropriate metal hydroxides to afford the corresponding salts. In some cases, the polymers were isolated as the free acids prior to conversion to the metal salts.



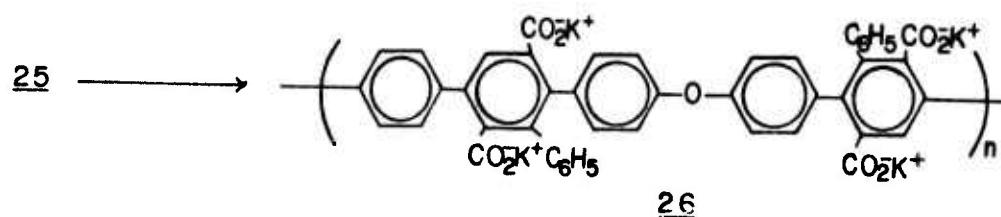
The carboxylated polyphenylene 24 ( $\eta_{\text{inh}} = 0.80$ , 0.25 g/dl in *sym*-tetrachloroethane at 30°C) was stirred for 56 hr in a 28.6% solution of potassium hydroxide in ethylene glycol heated at reflux. Acidification of the reaction mixture afforded polymer 25. The polymer



is soluble in acetone, alcohols, and DMSO and has an inherent viscosity of 0.69 (0.250 g/dl in DMSO at 30°C). Thin films can be cast from DMSO that show infrared absorptions characteristic of the model compounds 21 and 23 (Figure 7). Thermogravimetric analyses of pellet samples of 25 show an initial weight loss at 320°C in air and at 355°C in nitrogen. In nitrogen after the initial 25-30% weight loss, the polymer loses very little additional weight (4-5%) to 1000°C (Figure 8). Isothermal aging studies on a thin film at 265°C in air showed a rapid decrease in the OH absorption at 3000  $\text{cm}^{-1}$  accompanied by a sharpening of

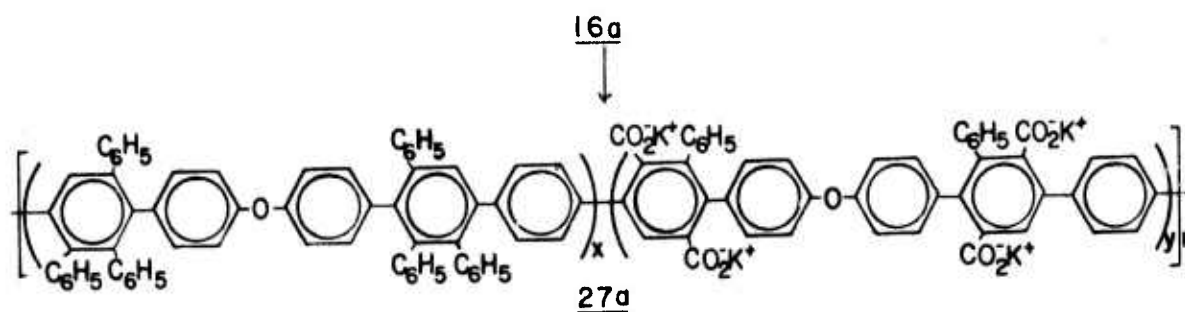
carbonyl absorption at  $1725\text{ cm}^{-1}$ . After 4 hr the OH absorption had completely disappeared, and a shoulder had appeared on the carbonyl absorption band (Figure 9). Evidently, crosslinking occurred through the formation of anhydride linkages. The infrared spectrum of the heat treated polymer does not show any aliphatic C-H stretching absorptions. This indicates that the hydrolyzed polymer contains no residual ester substituents. (The pendent ester substituents of polymer 24 are stable for at least 8 hr in air at  $265^\circ\text{C}$ ).<sup>1</sup> Thus, the hydrolysis of 24 under the conditions employed is quantitative.

A sample of polymer 25 in absolute methanol was neutralized with 0.1N potassium hydroxide to afford the potassium salt 26. The potassium



ionomer is soluble in water and alcohols and has an inherent viscosity of 0.96 (0.250 g/dl in  $\text{H}_2\text{O}$  at  $30^\circ\text{C}$ ). The infrared spectrum of a thin film cast from absolute methanol shows a reduced OH absorption at  $3250\text{ cm}^{-1}$ , a reduced acid carbonyl absorption at  $1710\text{ cm}^{-1}$ , and a new absorption at  $1600\text{ cm}^{-1}$ , characteristic of the carboxylate anion (C-O stretch)<sup>14</sup> (Figure 10). This indicates that the neutralization of the acid groups, although not 100% complete, was substantial. Films prepared from this ionomer are extremely brittle, which is indicative of their high crosslink density. Thermogravimetric analyses of 26 in air and nitrogen atmospheres show an initial 14% weight loss between 30 and  $300^\circ\text{C}$ . The weight loss was reduced to 4% when the polymer was dried at  $200^\circ\text{C}$  for 4 hr under nitrogen (Figure 11). Evidently, the polymer is very hygroscopic due to potassium hydroxide trapped in the polymer matrix.

A sample of the carboxylated phenylated-polyphenylene 16a was then stirred for 26 hr in a 5.5% solution of potassium hydroxide in ethylene glycol heated at reflux. The potassium ionomer 27a, which precipitated from the reaction mixture, is soluble in DMSO but not in toluene, chloroform, or alcohols. Thin films can be cast from DMSO that are flexible, tough, water-white, and transparent. The infrared spectra of the films indicate that the ionomer does contain some residual ester substituents (Figure 12). Thermogravimetric analysis in a nitrogen atmosphere show an initial weight loss of 6% between 370-550°C (Figure 13).

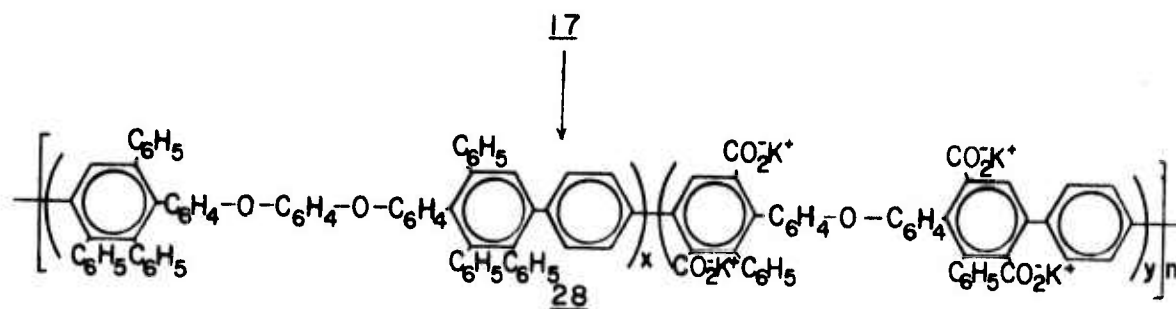


In order to determine the degree of hydrolysis when polymer 16a is subjected to hydrolysis conditions, several films of the polymer were prepared with different thicknesses (0.003 to 0.005 cm). A calibration curve of film thickness vs. the intensity of the corresponding ester carbonyl absorption at  $1735\text{ cm}^{-1}$  was then prepared (Figure 14). The degree of hydrolysis under the conditions described above was found to be 82% by correlating the carbonyl absorption of a film of the hydrolyzed polymer with the calibration curve. Samples of polymer 16a were also hydrolyzed in 19 and 38% solutions of potassium hydroxide in refluxing m-cresol to afford polymers that are 70 and 77% hydrolyzed, respectively (Table 2).

Polymer 16b was also hydrolyzed in a 5.5% solution of potassium hydroxide in refluxing ethylene glycol. In this case, the resulting ionomer 27d retained solubility in toluene and chloroform. The infrared spectrum of a thin film cast from chloroform indicated that only partial hydrolysis had occurred (Figure 15). Hence, a calibration curve of polymer film thickness vs. the intensity of the corresponding ester carbonyl absorption at  $1735\text{ cm}^{-1}$  was also prepared for this polymer

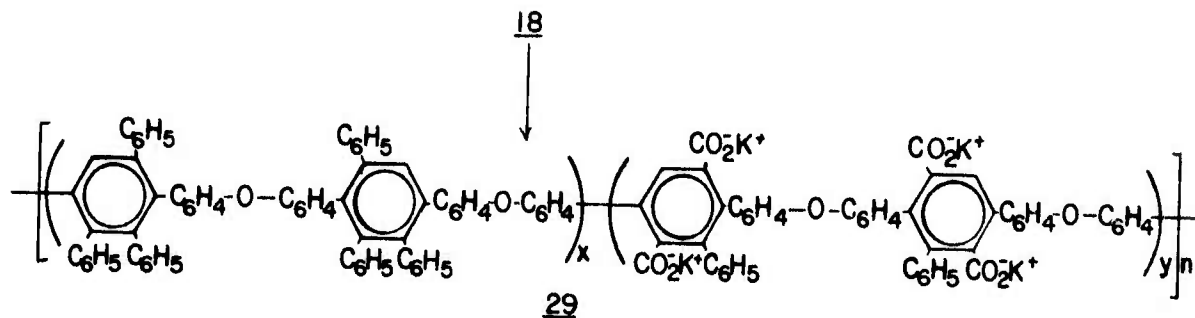
(Figure 16). Using this curve the degree of hydrolysis under the conditions described was determined to be approximately 50%. Interestingly, this corresponds to the exact percentage of carboxylate groups that are less sterically hindered. Polymer 16b was 100% hydrolyzed with a potassium hydroxide complex of dicyclohexyl-18-crown-6<sup>15</sup> in refluxing toluene (Table 2). The crown ether reagent, however, could not be completely removed from the resulting ionomer.

Treatment of the carboxylated phenylated-polyphenylene 17 with potassium hydroxide in refluxing ethylene glycol afforded the potassium salt 28. This ionomer is insoluble in common organic solvents, in contrast to the solubilities displayed by 27a-f. The biscyclopentadienone

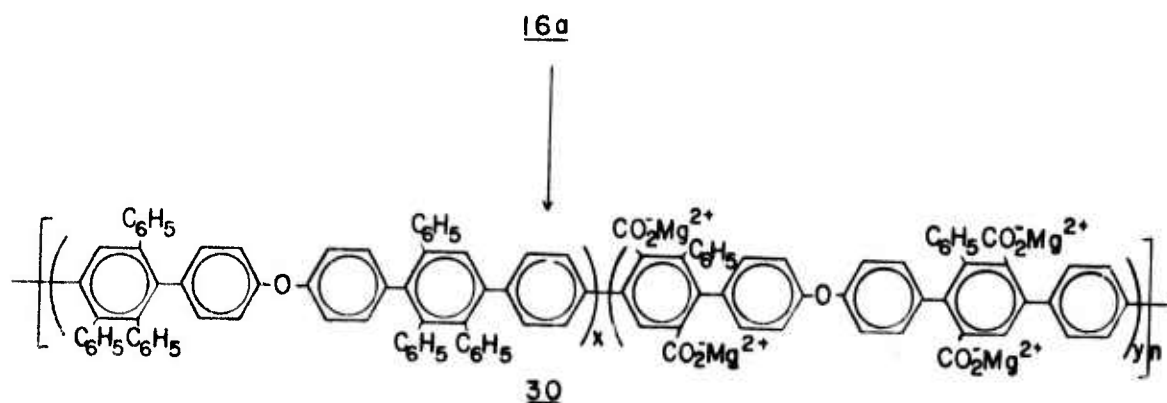


10, which contains the triphenyl diether linkage and was one of the monomers used to prepare polymer 17, is also considerably less soluble than similar biscyclopentadienones. This indicates that the triphenyl diether linkage is responsible for the reduction in solubility. This absorption of water was probably again due to potassium hydroxide trapped in the polymer matrix (Figure 17).

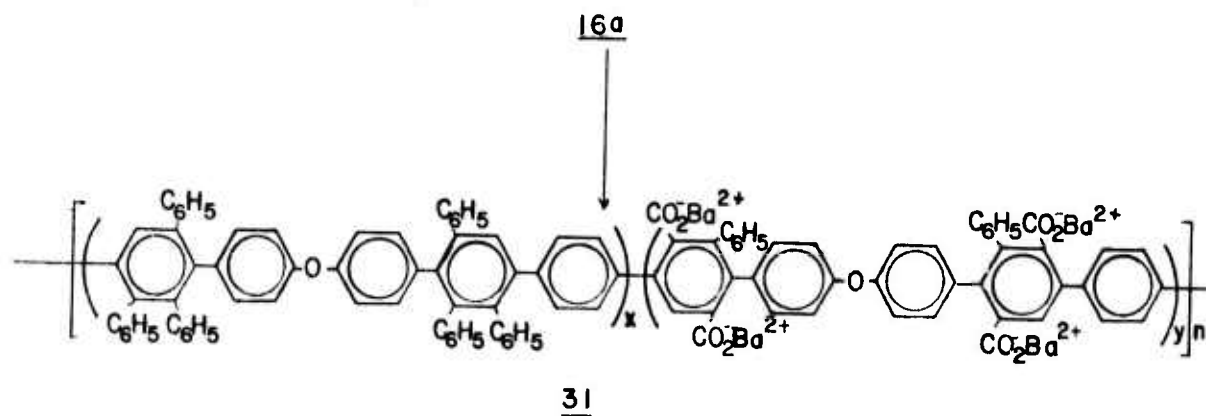
The potassium ionomer 29 was prepared by hydrolysis of polymer 18 in refluxing ethylene glycol containing potassium hydroxide. Ionomer 29 is soluble in DMSO and has an inherent viscosity of 1.0 (Table 2). Thermogravimetric analysis in a nitrogen atmosphere show an initial weight loss of 6% between 370-550°C (Figure 13).



The aromatic ionomer 30 was prepared by the hydrolysis of polymer 16a in refluxing *m*-cresol containing magnesium methoxide. The polymeric salt, which is completely insoluble in common organic solvents, shows a weak transition near 300°C (TMA penetration). This is comparable to the temperature at which the corresponding potassium ionomer undergoes a transition ( $\approx 312^\circ\text{C}$ ). Softening under load measurements, however, show that this transition is considerably weaker than that undergone by the potassium ionomer.



The hydrolysis of 16a with barium hydroxide in refluxing ethylene glycol provided the aromatic barium ionomer 31. The polymer is also insoluble in common organic solvents. Thermogravimetric analysis show that 31 is by far the most thermally stable ionomer prepared. The material shows no weight loss until near 500°C (Figure 19).



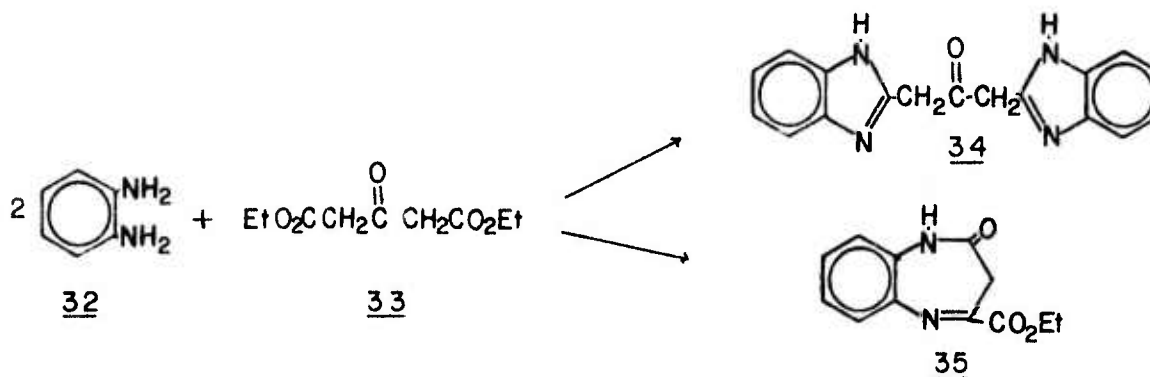




## 2. Preparation of Polyphenylenes Containing Aromatic Heterocyclics

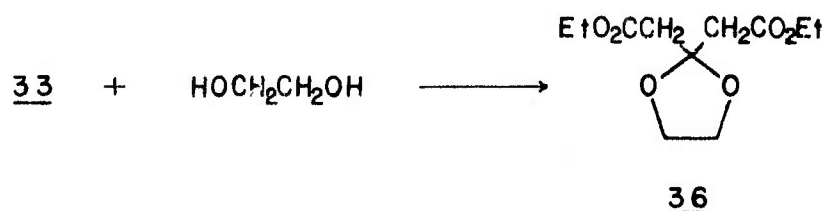
Thermally-stable phenylated polyphenylenes have been prepared that are soluble in common organic solvents.<sup>7</sup> However, due to their lack of polarity, these materials display poor adhesive properties. In order to increase the polyphenylenes' adhesion to fibers and metals, a project was carried out to incorporate heterocyclic rings in a polyphenylene system.

Our initial approach involved the preparation of benzimidazole-substituted biscyclopentadienone monomers. Various routes to 1,3-bis(2-benzimidazole)-2-propanone (34), which was to be condensed with tetra-ketones to afford biscyclopentadienones, were investigated. The reaction of *o*-phenylenediamine (32) with diethyl 1,3-acetonedicarboxylate (33) neat or in acetic acid did not afford 34 but instead gave high yield of compound 35. The reaction was also carried out in polyphos-



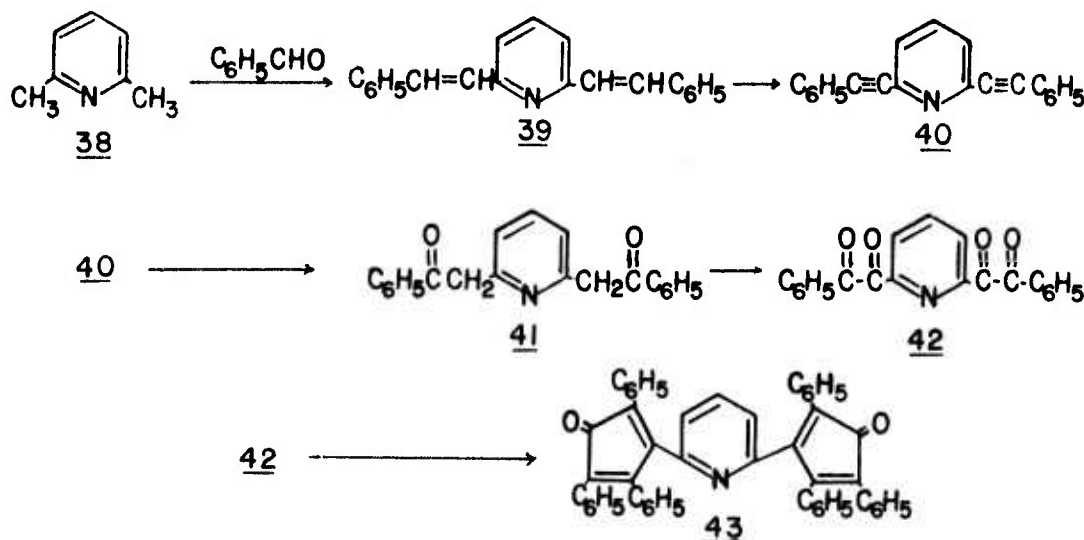
phoric acid to yield a crude product that displayed infrared absorptions characteristic of benzimidazoles. However, all attempts to purify this product were unsuccessful.

In an effort to block the formation of compound 35, the ketone carbonyl of 33 was converted to the corresponding ethylene ketal 36. Treatment of 36 with 32 in sulfolane yielded a waxy, white product that also displayed infrared absorptions



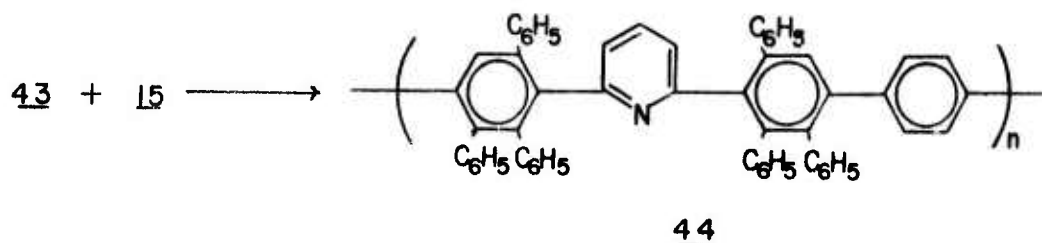
characteristic of benzimidazoles. All attempts to purify this product were also unsuccessful.

The synthesis of a biscyclopentadienone containing a pyridine nucleus was then investigated. The biscyclopentadienone 43 was prepared from lutidine (38) according to the following synthetic route.



The first three steps were carried out according to the known procedure<sup>16,17</sup> to afford the diketone 41 in good yield. Oxidation of 41 with selenium dioxide yielded the tetraketone 42, which was condensed with diphenylacetone to afford the biscyclopentadienone 43. The dark-purple monomer was purified by chromatography on neutral alumina with toluene: ether.

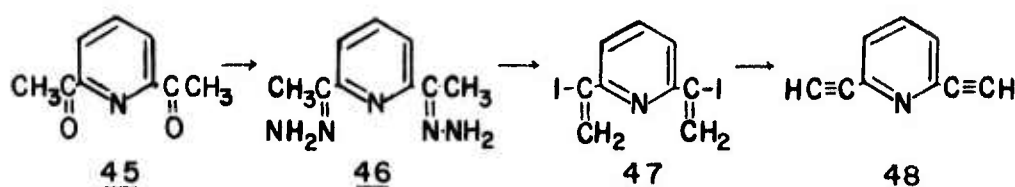
Polymerization of 43 with *p*-diethynylbenzene (15) in chlorobenzene contained in a sealed tube afforded the polypyridine 44. The polymer



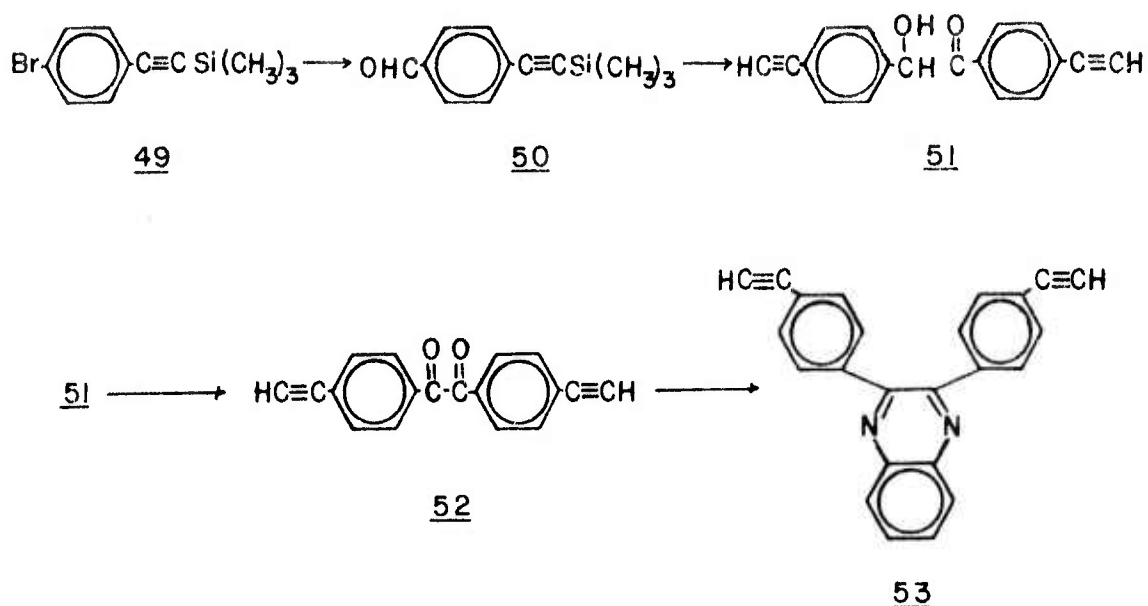
is soluble in pyridine and chlorinated hydrocarbons and has an inherent viscosity of 0.41. Thermogravimetric analyses of pelletized samples show major weight losses at 570°C in both air and nitrogen atmospheres (Figure 20).

A sample of polymer 44 was treated with anhydrous hydrogen chloride in *sym*-tetrachloroethane to afford the corresponding hydrochloride salt. The salt was isolated by precipitation in petroleum ether. Thermogravimetric analysis of the hydrochloride shows a 4% weight loss between 240 and 570°C, which corresponds closely to the loss of one hydrogen chloride molecule per repeat unit (Figure 21). The polymeric salt is soluble in chlorinated hydrocarbons and has an inherent viscosity of 0.63.

An alternate approach to the incorporation of heterocyclics in the polyphenylene backbone involved the preparation of diethynyl-substituted heterocyclic monomers. The synthesis of 2,6-diethynylpyridine (48) from 2,6-diacetylpyridine (45) was attempted by the reaction sequence described for the preparation of the dialkyne monomer 6. The reaction of 45 with aqueous hydrazine gave the dihydrazone 46 in 91% yield. Treatment of 46 with iodine, however, produced an intractable tar.



The synthesis of the diethynyl-substituted quinoxaline 53 was attempted by the following reaction scheme. The silane 49 was prepared from *p*-bromoacetophenone according to the known procedure.<sup>18</sup> The reaction of 49 with magnesium in THF gave the corresponding grignard reagent, which was allowed to react with DMF<sup>19</sup> to provide the benzaldehyde 50. This aldehyde, however, failed to undergo a benzoin condensation when treated with potassium cyanide.

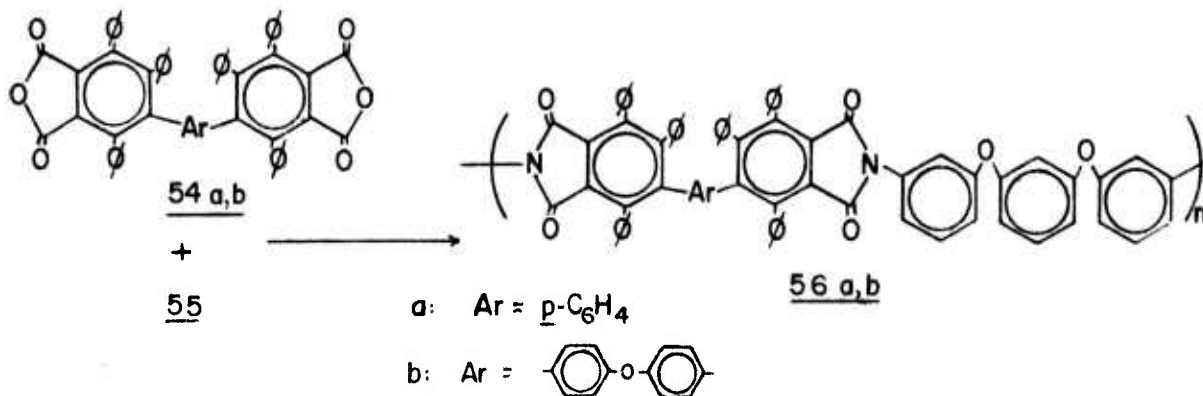


### 3. Synthesis and Modification of Phenylated Polyimides

As stated in the INTRODUCTION, the phenylated polyimides were to be modified so as to provide thermally-stable laminating resins that could be crosslinked without the evolution of volatile materials. Since the crosslinking mechanism selected involved the thermal polymerization of pendent ethynyl groups, research was carried out to lower the polyimide glass transition temperature below 250°C. An investigation of the synthesis and polymerization of ethynyl-substituted diamine monomers was also carried out.

#### a. Preparation of phenylated polyimides with low glass transition temperatures

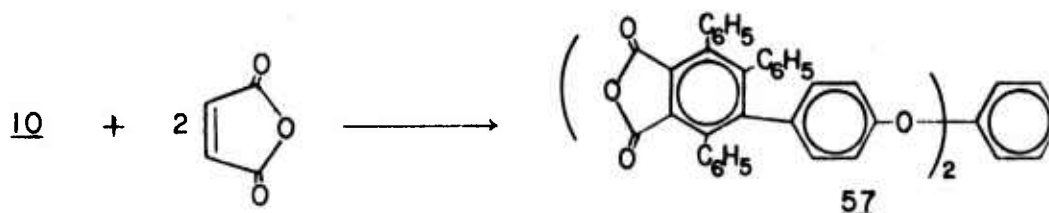
The phenylated dianhydrides 54a and b<sup>2</sup> were polymerized with 1,3-bis(3-aminophenoxy)benzene (55) in refluxing m-cresol containing



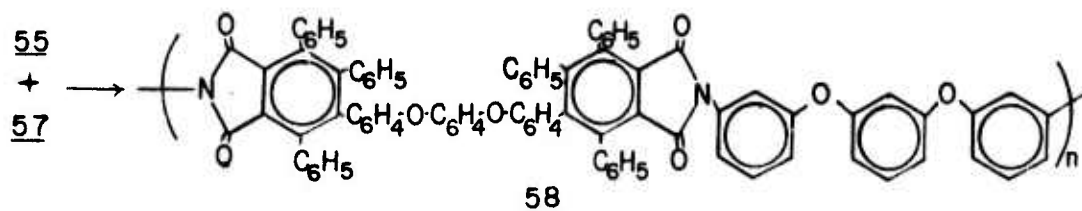
isoquinoline. The water that evolved from the reactions was removed by distillation. The white polymers 56a and b were isolated in nearly quantitative yields by precipitation with absolute ethanol. The polymers were then heated under vacuum at 250°C for 4 hr to insure complete conversion of the intermediate polyamic acid to the polyimide.

The polyimides 56a and b are soluble in chlorinated hydrocarbons and have intrinsic viscosities of 1.22 and 0.75, respectively. The glass transition temperatures of these polymers are 280 and 261°C, respectively. Thermogravimetric analyses of the polymers in helium show a major weight loss at 570°C (Figures 22 and 23).

Since the glass transition temperatures of polymers 56a and b were above 250°C, the synthesis of a new, more-flexible, phenylated dianhydride monomer was carried out. The reaction of the biscyclopentadienone 10 with maleic anhydride followed by dehydrogenation with bromine provided the dianhydride 57.



Polymerization of 57 with the diamine 55 in refluxing *m*-cresol containing isoquinoline afforded the polyimide 58. The polyimide was subsequently heated at 300°C under vacuum to insure complete



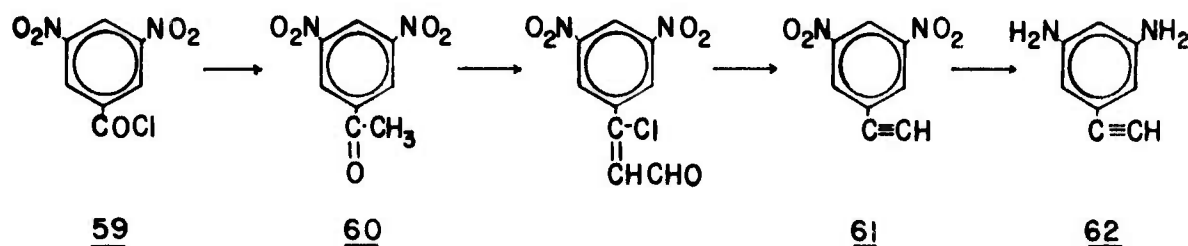
imidization. The polymer underwent viscous flow during the heat treatment. Thermal mechanical analysis employing a penetration mode shows initial penetration at 160°C with maximum penetration occurring near 238°C. This indicates that the polymer can be processed below 250°C. The off-white polyimide is very soluble in chloroform, forms slightly-



yellow films, and has an inherent viscosity of 1.00. Thermogravimetric analyses of pelletized samples show 5% weight losses at 545 and 555°C in air and nitrogen atmospheres, respectively (Figure 24).

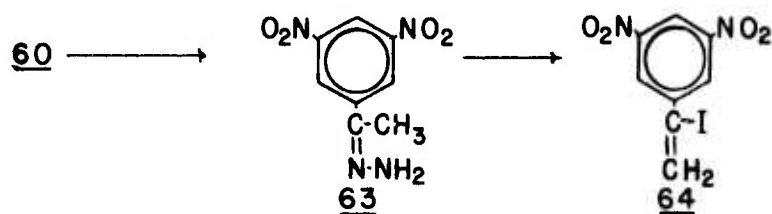
b. Synthesis of ethynyl-substituted diamines

The synthesis of 3,5-diaminophenylacetylene (62) was attempted by the following reaction route. The reaction of 3,5-dinitrobenzoyl



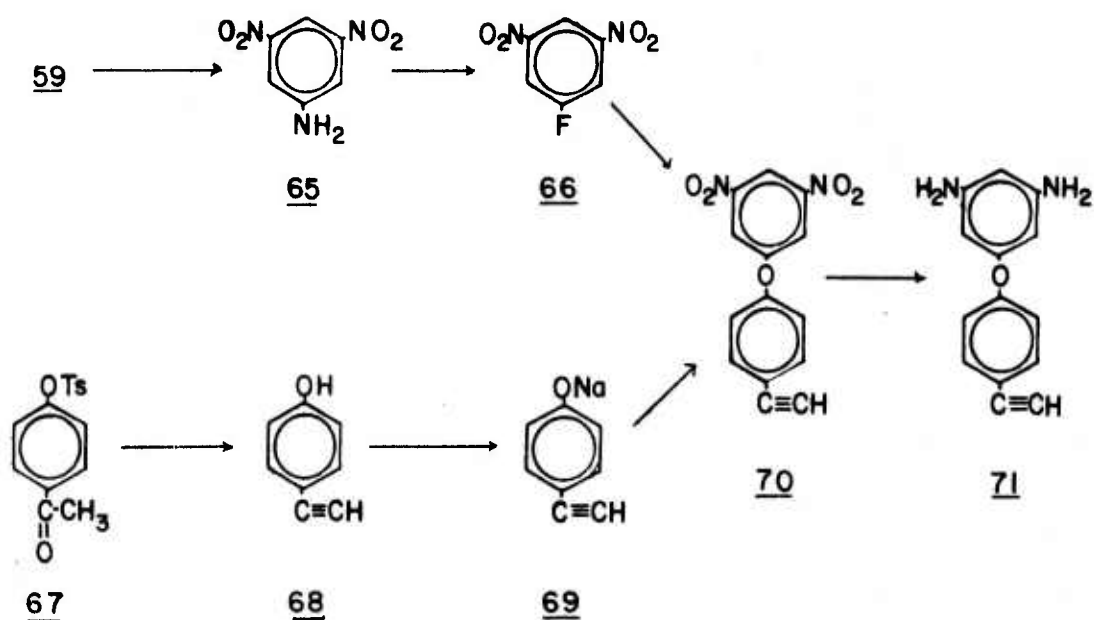
chloride with diethyl malonate followed by thermal decarboxylation yielded 3,5-dinitroacetophenone (60).<sup>20</sup> Treatment of 60 with a DMF/ $\text{POCl}_3$  complex provided a dark-red solid.<sup>21</sup> Attempts to purify this solid, however, were unsuccessful. The reaction of the crude product with base did not afford the phenylacetylene 61.

The following reaction sequence was also employed in an alternate approach to the synthesis of 62. Treatment of 60 with aqueous hydra-

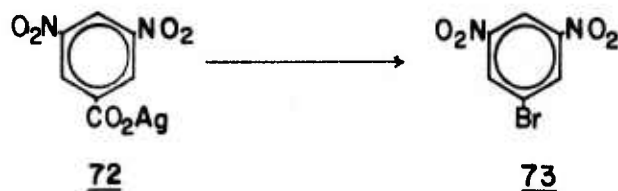


zine afforded the hydrazone 63. The reaction of 63 with iodine, however, did not yield compound 64.

The preparation of 4-(3,5-diaminophenoxy)phenylacetylene (71) was attempted by the following synthetic scheme. Treatment of 59 with sodium azide afforded 3,5-dinitrobenzoyl azide.<sup>22</sup> The azide was heated in sulfuric acid to yield 3,5-dinitroaniline (65). Diazotization of 65 followed by treatment with sodium fluoroborate, however, afforded a very low yield of 66.<sup>22</sup> Hence, this intermediate was replaced in the synthetic route with 3,5-dinitrobenzene (73).

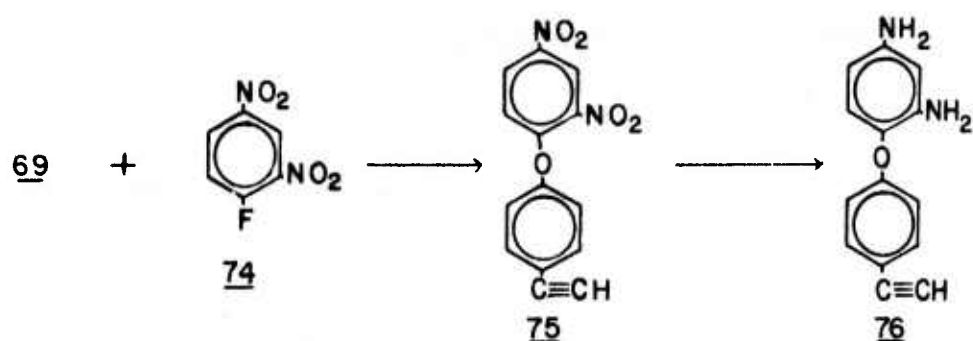


Compound 73 was prepared by a Hunsdiecker reaction. Thus, treatment of the silver salt 72 with bromine afforded a 58% yield of 73.<sup>22</sup>



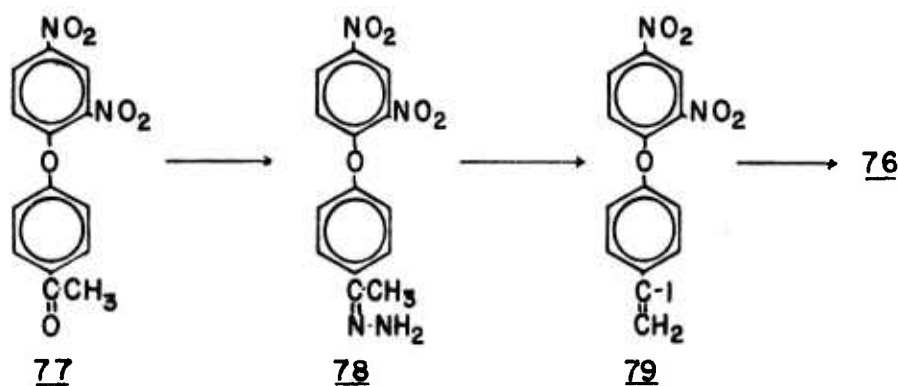
The reaction of the tosylate of p-hydroxyacetophenone (67) with a DMF/ $\text{POCl}_3$  complex followed by treatment with base provided the phenylacetylene 68. Compound 68 was hydrolyzed with potassium hydroxide in absolute methanol to afford the sodium salt of 4-ethynylphenol (69). The reaction of 69 with 73 in the presence of cuprous chloride, however, did not afford compound 70. In fact, starting material was recovered unchanged. An extensive study of reaction conditions in which solvent, temperature, and reaction time were varied failed to effect the coupling of 69 with 73.

The synthesis of 4-(2,4-diaminophenoxy)phenylacetylene (76) was attempted by the following reaction route. Treatment of 69 with



2,4-dinitrofluorobenzene (74) in DMF provided the phenylacetylene 75. Several attempts to reduce compound 75 employing several different reducing agents, however, failed to afford reasonable yields of the diamine 76. Reduction with sodium hydrosulfite did give a very low yield of a crude solid that displayed infrared absorptions characteristic of amines and alkynes. All attempts to isolate additional diamine from the reaction mixture were unsuccessful.

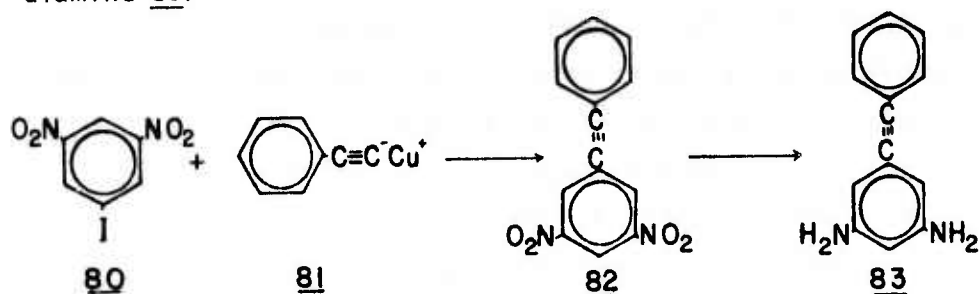
An alternate synthesis of 76 via the following reaction scheme was then attempted. The reaction of 4-(2,4-dinitrophenoxy)aceto-



phenone (77) with aqueous hydrazine gave a 60% yield of the hydrazone 78. Treatment of 78 with iodine afforded a low yield of crude 79, which resisted purification. The reaction of crude 79 with base did not give compound 76.

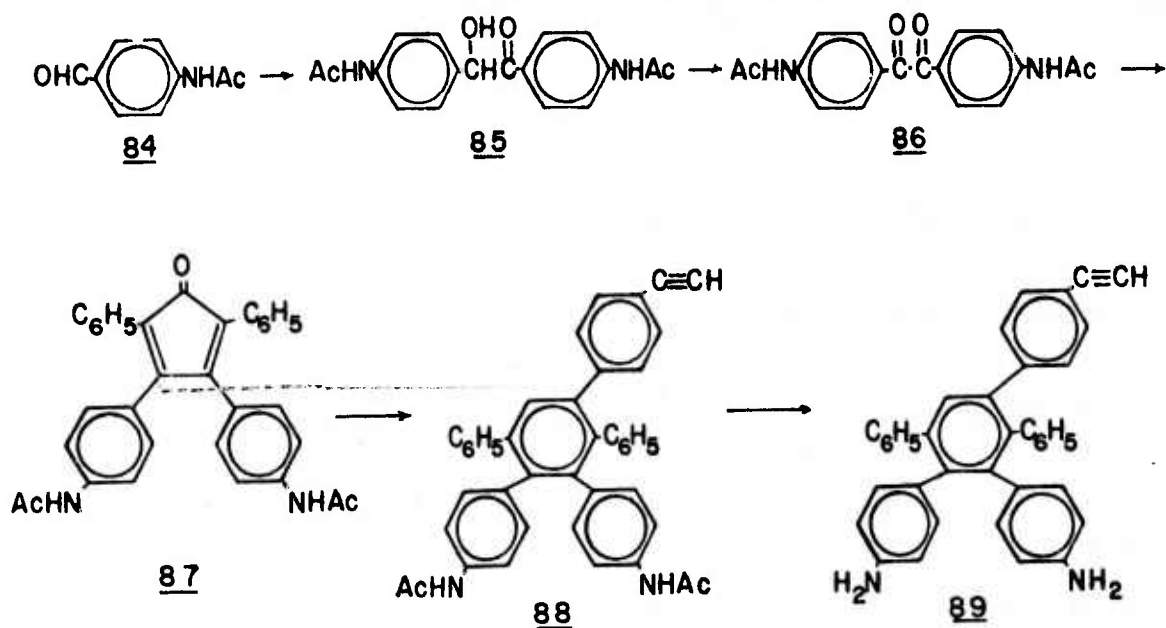
The synthesis of 3,5-diaminodiphenylacetylene (83) was attempted by the following reaction scheme. Treatment of 3,5-dinitroiodobenzene (80)<sup>24</sup> with cuprous phenylacetylide (81) in hexamethylphosphoramide (HMPA) afforded a 75% yield of compound 82. Reduction of 82 with

various reducing agents, however, produced only low yields of the impure diamine 83.



A similar scheme was used in an attempted preparation of 2,4-diaminodiphenylacetylene. In this case, treatment of 2,4-dinitroiodobenzene with 81 in HMPA gave a 93% yield of 2,4-dinitrodiphenylacetylene. However, all attempts to reduce the dinitro compound resulted in low yields of impure diamine.

The ethynyl-substituted diamine 89 was prepared by the following synthetic scheme. Treatment of *p*-acetamidobenzaldehyde (84)

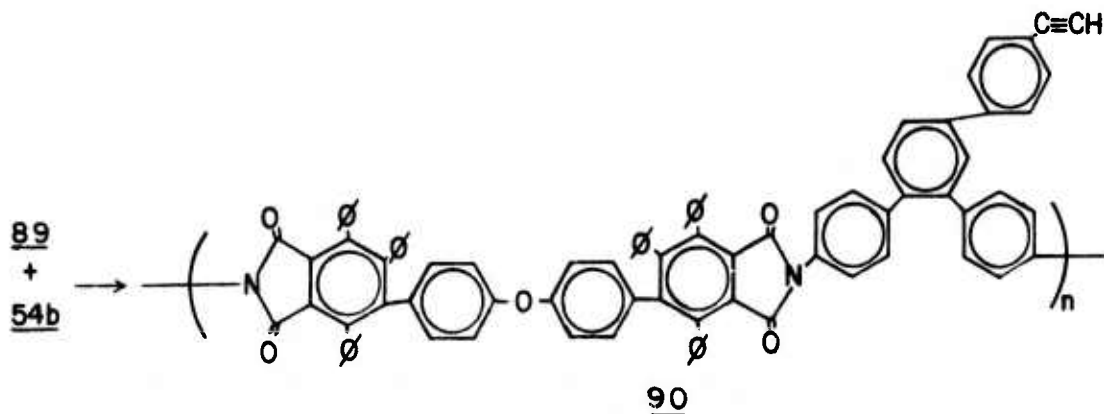


with potassium cyanide provided the benzoin 85, which was oxidized with copper sulfate to afford the benzil 86.<sup>25</sup> The base-catalyzed condensation of 86 with diphenylacetone yielded the cyclopentadienone 87. The dark magenta diene underwent a Diels-Alder addition with excess

p-diethynylbenzene to give compound 88, which upon hydrolysis afforded the diamine 89.

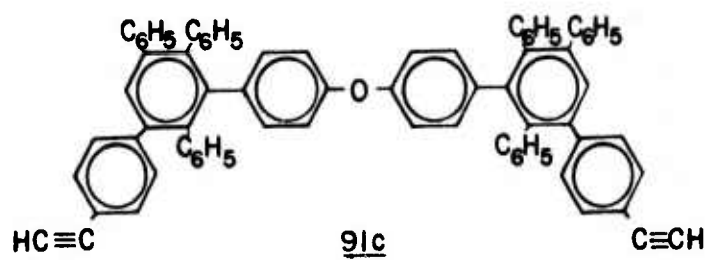
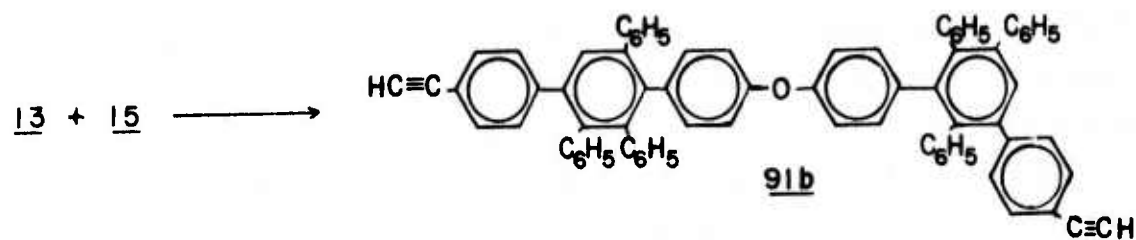
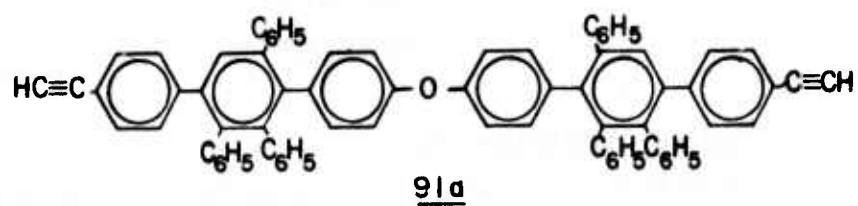
c. Polymerization of ethynyl-substituted diamines

The diamine 89 was polymerized with the phenylated dianhydride 54b in *m*-cresol containing isoquinoline to afford the polyimide 90. The polymer is soluble in chlorinated hydrocarbons and can be cast into thin, brittle films. The DSC spectrum shows a strong exotherm near 250°C, which is indicative of the polymerization of the pendent ethynyl substituents. The slow heating of a sample of 90 to 250°C resulted in a completely insoluble material. Thermogravimetric analyses show that the polymer loses only 2-3% of its weight before 400°C (Figure 25).



4. Acetylene-Terminated Polyphenylene Oligomers

As part of the preceding study that was essentially aimed at the preparation of thermally-stable resins that can be crosslinked without the evolution of volatile materials, the synthesis and polymerization of acetylene-terminated polyphenylenes were investigated. The reaction of the biscyclopentadienone 13 with excess p-diethynylbenzene (15) afforded the isomeric oligomers 91a-c. The DSC spectrum of this mixture shows a strong exotherm with a maximum near 250°C (Figure 26). When a powdered sample was heated at 250°C for 3 hr under nitrogen, the mixture became completely insoluble but did not darken. Thermogravimetric analyses show no weight loss until near 550°C in both air and nitrogen atmospheres (Figure 27). This indicates that the acetylene-terminated polyphenylene oligomers undergo crosslinking near 250°C without the evolution of volatiles.



### SECTION III EXPERIMENTAL

#### 1. Physical Determinations

Infrared spectra were obtained on Perkin Elmer Model 457 and Model 621 spectrophotometers. Proton NMR spectra were obtained with a Varian HA-60-IL NMR spectrometer. All samples were run at concentrations of 10-20% using tetramethylsilane as an internal standard. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana. Thermogravimetric analyses were carried out on a DuPont 950 Thermogravimetric Analyzer with a heating rate of 5°C/min. Inherent viscosities were measured in a Cannon-Ubbelohde Microdilution Viscometer No. 75. Glass transition temperatures were determined by Dr. G. H. Ehlers at AFML, WPAFB. The values reported were obtained by correlating DSC and TMA data.

#### 2. Synthesis and Modification of Carboxylated Polyphenylenes

##### a. 4,4'-Diacetyldiphenylether dihydrazone (4)

A mixture of 16.0 g (0.063 mol) of 4,4'-diacetyldiphenylether, 26 ml (0.5 mol) of 65% aqueous hydrazine, 75 ml triethylamine and 200 ml ethanol was refluxed for 4 hr. The reaction mixture was cooled in ice to yield 12.5 g (70%) of pure white plates: mp 142-143°; ir (KBr) 3300  $\text{cm}^{-1}$  (m, N-H).

##### b. 4,4'-Bis( $\alpha$ -iodoethenyl)diphenylether (5)

A mixture of 12.5 g (0.044 mol) of 4,4'-diacetyldiphenyl ether dihydrazone, 750 ml tetrahydrofuran and 375 ml of triethylamine under  $\text{N}_2$  was treated dropwise with a solution of 55.0 g of iodine (0.22 mol as  $\text{I}_2$ ) in 150 ml tetrahydrofuran. When approximately one-half of the solution was added, a precipitate of triethylammonium iodide formed. After stirring for 1 hr, the amine salt was removed by filtration. The reaction mixture was then concentrated under reduced pressure, dissolved in methylene chloride, washed with 2N hydrochloric acid and 5% sodium thiosulfate solution, and dried (anh  $\text{MgSO}_4$ ). The crude oily product obtained on removal of the solvent crystallized on addition of a small amount of absolute ethanol. Recrystallization from absolute ethanol yielded 14.5 g (70%) of a tan solid mp 109-110°.



c. 4,4'-Diethynyldiphenylether (6)

A mixture of 8.2 g (0.017 mol) of 4,4'-bis( $\alpha$ -iodoethenyl) diphenylether, 47 g potassium hydroxide, and 550 ml of ethanol was refluxed for 4 hr. The solvent was then removed under reduced pressure. Water (700 ml) was then added to the residue and the resulting suspension stirred for 1 hr. The crude tan solid was collected and purified by vacuum sublimation to yield 3.2 g (85%) of pure white crystals: mp 76-77° (lit.<sup>8</sup> 77-77.5°); ir (neat) 3280 (s,  $\equiv$ C-H) and 2270  $\text{cm}^{-1}$  (w,  $\text{C}\equiv\text{C}$ ).

d. 1,4-Diphenoxybenzene (7)

The synthesis of this compound by the copper-catalyzed coupling of 4-bromodiphenylether with potassium phenoxide was carried out according to the known procedure<sup>26</sup> to afford a 97% yield of tan solid: mp 71-73° (lit.<sup>27</sup> 74°).

e. 1,4-Bis(p-phenylacetylphenoxy)benzene (8)

A solution of 1,4-diphenoxybenzene (19.0 g, 0.07 mol) and phenylacetylchloride (24.0 g, 0.15 mol) in 185 ml of methylene chloride was slowly added over 4 hr to a slurry of anhydrous aluminum chloride (21.5 g, 0.16 mol) in 135 ml of methylene chloride at 0-5°. After the addition was complete, the dark brown mixture was stirred at room temperature overnight and then poured into a mixture of ice (1 kg) and concentrated hydrochloric acid (175 ml). The organic phase was separated and washed successively with water, aqueous sodium carbonate, and water. After drying over anhydrous magnesium sulfate, the solution was concentrated under reduced pressure and cooled to yield 17.5 g (50%) of an off-white solid: mp 200-203°; ir(KBr) 1703  $\text{cm}^{-1}$  (s,  $\text{C}=\text{O}$ ); nmr ( $\text{CDCl}_3$ )  $\delta$  4.19 (s, 4H) and 6.7-8.1 ppm (m, 22H).

Anal. Calcd for  $\text{C}_{34}\text{H}_{26}\text{O}_4$ : C, 81.90; H, 5.26.

Found: C, 81.69; H, 5.20.

f. 1,4-Bis(p-phenylglyoxalylphenoxy)benzene (9):

A mixture of 5.00 g (0.010 mol) of 1,4-bis(p-phenylacetylphenoxy)benzene and 2.50 g (0.022 mol) selenium dioxide in 50 ml of glacial acetic acid was heated at reflux for 18 hr. The black reaction mixture was filtered hot, and the filter cake was washed twice with 25 ml of hot acetic acid. The combined filtrates were allowed to cool,

and the yellow solid that precipitated was collected by filtration. The solid was washed with ethanol and air dried to afford 5.0 g (95%) of crude product. Chromatography on acid-washed alumina with chloroform yielded 3.30 g of a bright yellow solid: mp 157-158°; ir (KBr)  $1689\text{ cm}^{-1}$  (s, C=O)

Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{O}_6$ : C, 77.55; H, 4.21.

Found: C, 77.29; H, 4.41.

g. 1,4-Bis(p-2,4,5-triphenyl-3-oxocyclopentadienylphenoxy)benzene (10)

To a stirred suspension of 2.166 g (4.11 mmol) of 1,4-bis(p-phenylglyoxalylphenoxy)benzene and 1.886 g (8.97 mmol) of 1,3-diphenylacetone in 11 ml of ethylene glycol heated at 140-150° was slowly added 1.5 ml of N-benzyltrimethylammonium hydroxide (40% in methanol). After the deep purple suspension was heated an additional 1 hr at 140-150°, the mixture was cooled to room temperature and poured into 250 ml of 95% ethanol. The purple solid was collected by filtration and air dried. The crude product was chromatographed on neutral alumina with toluene:ether (9:1). Removal of the solvent under reduced pressure yielded 0.88 g (25%) of a deep purple solid: mp 296-297°; ir (KBr)  $1735\text{ cm}^{-1}$  (s, C=O).

Anal. Calcd for  $\text{C}_{64}\text{H}_{42}\text{O}_4$ : C, 87.85; H, 4.84.

Found: C, 87.57; H, 4.94.

The above procedure was repeated with bromobenzene as the solvent. Although the reactants were completely soluble in hot bromobenzene, the results (25% yield) were identical.

h. Biscyclopentenone salt 11

To a suspension of 4.00 g (7.6 mmol) of 1,4-bis(p-phenylglyoxalylphenoxy)benzene and 5.0 ml (16.0 mmol) of diethyl 1,3-acetonedicarboxylate in 200 ml of refluxing absolute ethanol was slowly added 30 ml of a 7% solution of sodium ethoxide in absolute ethanol. The reaction mixture slowly changed from a light to a very bright yellow. The suspension was heated at reflux for an additional 2 hr, cooled, and filtered to give a quantitative yield of the biscyclopentenone salt 11: mp >300°; ir (KBr)  $1732\text{ cm}^{-1}$  (s, C=O).

i. 1,4-Bis(p-2,5-diethoxycarbonyl-4-phenyl-3-oxocyclopentadienyl-phenoxy)benzene (12)

A solution of 4.0 g of the disodium salt 11 in 50 ml of glacial acetic acid was added slowly to 800 ml of water with vigorous stirring to yield 3.7 g (95%) of the corresponding dihydroxy biscyclopentenone: mp 75° (dec); ir (KBr) 3490 (s, br, OH) and 1745  $\text{cm}^{-1}$  (s, C=O).

To a solution of 3.7 g of the dihydroxy cyclopentenone in 25 ml of acetic anhydride was added 5 drops of concentrated  $\text{H}_2\text{SO}_4$ . The solution changed from light yellow to deep orange. Water was then added slowly to decompose the excess anhydride. The rate of addition was regulated so that the temperature of the reaction was maintained below 60°. The dark orange residue was chromatographed on silica gel with chloroform: ether (9:1). After the solvent was removed under reduced pressure, the residue was triturated with hexane to yield a bright orange powder: mp 172-175°; ir (KBr) 1725  $\text{cm}^{-1}$  (s, C=O).

j. Preparation of carboxylated phenylated-polyphenylene 16a

A mixture of 0.6263 g (0.8 mmol) of 3,3'-(oxydi-p-phenylene)bis[2,4,5-triphenylcyclopentadienone], 0.1534 g (0.2 mmol) of 3,3'-(oxydi-p-phenylene)bis[2,5-diethoxycarbonyl-4-phenylcyclopentadienone], and 0.1261 g (1.0 mmol) of p-diethynylbenzene was placed in a 100 ml polymerization tube with 5.0 ml of chlorobenzene. The contents of the tube were degassed by several freeze-thaw cycles at liquid temperature and then sealed under vacuum. Approximately 300 ml of xylene was added to a Parr pressure reactor, the polymerization tube placed inside, and the reactor was closed and heated at 110° for 18 hr. The temperature was then increased to 180° and the heating continued for an additional 18 hr. After the reaction had cooled to room temperature, the tube was opened and the reaction mixture poured into 500 ml of absolute ethanol. The precipitated polymer was filtered and reprecipitated from chloroform with absolute ethanol. The light pink polymer (0.6883 g, 81%) was dried under vacuum at 150° for 24 hr :  $\eta_{\text{inh}} = 0.33$  (0.250 g/dl in sym-tetrachloroethane at 30°); ir (film) 1745  $\text{cm}^{-1}$  (C=O).

The above procedure was repeated with the temperature of the second 18 hr cycle being increased to 220°. The polymer obtained was off-white and had an inherent viscosity of 0.77.

A similar procedure was followed for the preparation of polymer 16b to afford a material with  $\eta_{inh} = 0.49$ .

k. Preparation of carboxylated phenylated-polyphenylene 17

Polymer 17 was prepared from 1.545 mmol of the biscyclopentadienone 10, 0.370 mmol of 3,3'-(oxydi-*p*-phenylene)bis[2,5-diethoxycarbonyl-4-phenylcyclopentadienone], and 1.916 mmol of *p*-diethynylbenzene by the procedure described for the preparation of polymer 16a. The off-white polymer, which was obtained in nearly quantitative yield, was dried under vacuum at 110° for 72 hr :  $\eta_{inh} = 1.05$  (0.250 g/dl in *sym*-tetrachloroethane at 30°); ir (film) 1725  $\text{cm}^{-1}$  (C=O).

l. Preparation of carboxylated phenylated-polyphenylene 18

Polymer 18 was prepared from 2.40 mmol of 3,3'-(oxydi-*p*-phenylene)bis[2,4,5-triphenylcyclopentadienone], 0.60 mmol of 3,3'-(oxydi-*p*-phenylene)bis[2,5-diethoxycarbonyl-4-phenylcyclopentadienone], and 3.00 mmol of 4,4'-diethynyldiphenylether by the procedure described for the preparation of polymer 16a. The light pink polymer, which was obtained in nearly quantitative yield, was dried under vacuum at 110° for 48 hr:  $\eta_{inh} = 0.42$  (0.25 g/dl in *sym*-tetrachloroethane at 30°).

The procedure was repeated with the length of the second cycle being increased to 43 hr. The polymer obtained was white and had an inherent viscosity of 0.77.

m. Hydrolysis of diethyl 2,3,5-triphenylterephthalate (19)

Procedure 1

To a solution of 8.0 g (0.014 mol) of potassium hydroxide in 50 ml of absolute ethanol was added 1.80 g (0.004 mol) of diethyl 2,3,5-triphenylterephthalate. After the reaction mixture was heated a reflux for 24 hr, it was poured into 250 ml of water. The aqueous solution was acidified with dilute hydrochloric acid, and the white solid that formed was collected by filtration. The product was recrystallized from methanol-water and dried under vacuum at 110° for 18 hr to afford 1.1 g (65%) of white crystals, mp 189-191°. Infrared and nmr spectra indicated that only one ester group had been hydrolyzed: ir (KBr) 3050 (s, br, COOH) and 1700  $\text{cm}^{-1}$  (s, br, ester and acid C=O); nmr ( $\text{CDCl}_3$ -acetone- $\text{d}_6$ )  $\delta$  0.70 (t, 3,  $\text{CH}_3$ ), 3.70 (q, 2,  $\text{CH}_2$ ), 5.70 (br, 1, COOH), 7.07 (s, 10, ArH), 7.45 (m, 5, ArH), and 7.85 ppm (s, 1, ArH).

Anal. Calcd for  $\text{C}_{28}\text{H}_{22}\text{O}_4$ : C, 79.63; H, 5.21.  
Found: C, 79.24; H, 5.08.

### Procedure 2

To 10 ml of 0.5N potassium t-butoxide in DMSO was added 3.0 g (0.0067 mol) of diethyl 2,3,5-triphenylterephthalate. After the reaction mixture was allowed to stir for 12 hr at room temperature, it was poured into 250 ml of water. The solution was then acidified with dilute hydrochloric acid. The white solid that formed was collected by filtration, recrystallized from methanol-water, and dried under vacuum at 150° for 18 hr. A second recrystallization from methanol-water gave 2.2 g (79%) of white crystals: mp 190-191°.

### Procedure 3

To a solution of 28.0 g (0.6 mol) of potassium hydroxide in 125 ml of ethylene glycol was added 14.0 g (0.03 mol) of diethyl 2,3,5-triphenylterephthalate. The reaction mixture was heated at reflux with stirring for 4.5 hr. After the solution was allowed to cool, it was slowly added to 2l of water. The aqueous solution was then acidified with dilute hydrochloric acid. The white solid that formed was collected by filtration and recrystallized from acetic acid-water. The product was triturated with hot toluene to remove residual acetic acid and dried under vacuum at 110° overnight to afford 9.0 g (76%) of white crystals: mp 277-279°.

Anal. Calcd for  $C_{26}H_{18}O_4$ : C, 79.17; H, 4.60.  
Found: C, 79.30; H, 4.53.

Neutralization Equivalent Calcd for  $C_{26}H_{18}O_4$ : eq wt = 197.20  
Found: eq wt = 197.89

### n. 3,3",6,6"-tetraethoxycarbonyl-4,4",5,5"-tetraphenyl-p-terphenyl (21)

To a solution of 15.0 g (0.27 mol) of potassium hydroxide in 60 ml of ethylene glycol was added 8.0 g (0.0097 mol) of 3,3",6,6"-tetraethoxycarbonyl-4,4",5,5"-tetraphenyl-p-terphenyl. After the mixture had been heated at reflux with stirring for 1.5 hr, a white solid precipitated. The suspension was then allowed to cool and poured into 800 ml of water. The aqueous solution was acidified with dilute hydrochloric acid. The precipitate that formed was collected by filtration, air dried, and recrystallized from absolute ethanol to give 5.4 g (78%) of white crystals: mp 418-420° (dec).

Anal. Calcd for  $C_{46}H_{30}O_8$ : C, 77.76; H, 4.22.  
Found: C, 77.92; H, 4.20.

Neutralization Equivalent Calcd for  $C_{46}H_{30}O_8$ : eq wt = 177.61

Found: eq wt = 178.17

o. Hydrolysis of poly[2,2",5,5"-tetrakis(ethoxycarbonyl)-3,3"-diphenyl-p-quaterphenyl-4,4"-ylene] (24)

To a solution of 20.0 g (0.36 mol) of potassium hydroxide in 70 ml of ethylene glycol was added 2.7 g of polymer 24 ( $\eta_{inh} = 0.77$  dl/g). The mixture was heated at reflux with vigorous stirring for 56 hr. The solution was then cooled and added dropwise to a solution of 200 ml of concentrated hydrochloric acid in 1 l of water. The resulting precipitate was collected by filtration, air dried, and reprecipitated from acetone with benzene. The cream colored polymer was collected by filtration and dried under vacuum at  $110^\circ$  for 24 hr:  $\eta_{inh} = 0.84$  dl/g.

p. Preparation of potassium ionomer 26

The pH of a solution of 0.5 g of polymer 25 ( $\eta_{inh} = 0.69$ ) in 50 ml of absolute methanol was adjusted with 0.1N KOH in absolute methanol to a pH of 8. The solvent was then removed under reduced pressure and the resulting solid dried under vacuum at  $65^\circ$  to afford the ionomer:  $\eta_{inh} = 0.96$  (0.250 g/dl in  $H_2O$  at  $30^\circ$ ).

q. General procedure for the preparation of aromatic ionomers from carboxylated phenylated-polyphenylenes

A mixture of the polyphenylene, the appropriate base, and the selected solvent was heated at reflux for the designated time period. The suspension was then allowed to cool and poured into absolute ethanol. The ionomer was collected by filtration, reprecipitated from DMSO with absolute methanol (if soluble), and dried under vacuum at  $110^\circ$  for 48 hr (See Table 2).

3. Preparation of Polyphenylenes Containing Aromatic Heterocyclics

a. Reaction of diethyl 1,3-acetonedicarboxylate with o-phenylenediamine in acetic acid

To a solution of 2.04 g (0.02 mol) of diethyl 1,3-acetonedicarboxylate in 25 ml of glacial acetic acid was added 4.32 g (0.04 mol) of o-phenylenediamine. The mixture was heated to reflux during which time a white solid began to precipitate. After a few minutes the reaction mixture essentially solidified. The suspension was cooled and filtered. The crude product was recrystallized from absolute ethanol to yield white crystals: mp  $231-232^\circ$ ; ir (KBr) 3210, 3095 (NH, amide), 1720 (C=O, ester),

1685, 1660 (C=O, amide), and 1620  $\text{cm}^{-1}$  (NH, bend, amide); nmr ( $\text{CDCl}_3$ )  $\delta$  1.6 (t, 3,  $\text{CH}_3$ ), 3.5 (s, 2,  $\text{CH}_2$ ) 3.7 (s, 2,  $\text{CH}_2$ ), 4.4 (s, 2, ester  $\text{CH}_2$ ), 5.1 (s, 1, NH) and 7.5 ppm (m, 4, ArH).

When the above procedure was repeated with excess diethyl 1,3-acetonedicarboxylate as the solvent identical results were obtained.

b. Reaction of diethyl 1,3-acetonedicarboxylate and o-phenylenediamine in PPA

Polyphosphoric acid (125 g) was degassed at 100° with nitrogen for 18 hr. To the degassed solvent was added 10.1 g (0.05 mol) of diethyl 1,3-acetonedicarboxylate and 10.8 g (0.10 mol) o-phenylenediamine. After the solution was heated at 100° for 1 hr, the temperature was slowly raised to 160° and then maintained at this temperature for an additional 2 hr. The hot solution was poured into 1 l of water and the pH of the mixture adjusted to 7 with NaOH. Attempts to purify the dark precipitate that formed were unsuccessful. The infrared spectra of the crude product shows a broad band at 2400-3200  $\text{cm}^{-1}$ , characteristic of benzimidazole N-H stretching.

c. Ethylene ketal of diethyl 1,3-acetonedicarboxylate (36)

The acid catalyzed reaction of ethylene glycol with diethyl 1,3-acetonedicarboxylate as described<sup>28</sup> afforded the ketal 36: bp 115-120° (0.6 mm) [lit.<sup>28</sup> 162-164° (25 mm)].

d. Reaction of the ethylene ketal of diethyl 1,3-acetonedicarboxylate with o-phenylenediamine

A solution of 4.92 g (0.02 mol) of the ethylene ketal of diethyl 1,3-acetonedicarboxylate and 4.32 g (0.04 mol) o-phenylenediamine in 20 ml of sulfolane was degassed with nitrogen for 30 min and then heated under nitrogen at 180° for 18 hr. After the solution was allowed to cool, it was poured in 1 l of  $\text{H}_2\text{O}$ . The white, waxy solid that precipitated was collected by filtration. The infrared spectrum of the crude product shows a broad band between 3200-2400  $\text{cm}^{-1}$ . Attempts to purify this compound were unsuccessful.

e. 2,6-Distyrylpyridine (39)

The compound was prepared by the condensation of lutidine and benzaldehyde according to the known procedure<sup>16</sup> in 75% yield: mp 166-168° (lit.<sup>16</sup> 166.5°).



f. 2,6-Di-( $\beta$ -phenylethynyl)pyridine (40)

Treatment of 39 with bromine followed by debromination as described<sup>17</sup> provided compound 40 in 65% yield: mp 137-138° (lit.<sup>17</sup> 137-138°).

g. 2,6-Diphenacylpyridine (41)

The compound was prepared by the hydration of 2,6-di-( $\beta$ -phenylethynyl)pyridine according to the known procedure<sup>17</sup> in 68% yield: mp 84-85° (lit.<sup>17</sup> 90°).

h. 2,6-Diphenylglyoxalpyridine (42)

A solution of 3.0 g (0.01 mol) of 2,6-diphenacylpyridine, 2.4 g (0.022 mol) selenium dioxide and 55 ml of glacial acetic acid was heated to reflux for 18 hr. The acetic acid was then removed under reduced pressure and the resulting oil poured into 600 ml of water. The water layer was extracted with two 100 ml portions of chloroform. The chloroform layer was dried over anhydrous  $\text{MgSO}_4$ , reduced in volume and chromatographed on a dry silica gel column using chloroform as the eluent to yield 1.2 g (35%) of light yellow solid: m.p. 132-133°.

Anal. Calcd for  $\text{C}_{21}\text{H}_{13}\text{NO}_4$ : C, 73.46; H, 3.82; N, 4.08.

Found: C, 73.63; H, 3.71; N, 3.91.

i. 3,3'(2,6-Pyridinediyl)bis(2,4,5-triphenylcyclopentadienone) (43)

A solution of 2.0 g (5.8 mmol) of 2,6-diphenylglyoxalpyridine and 2.65 g (12.16 mmol) of benzyl ketone in 25 ml ethylene glycol was heat to 140°. To the hot solution was added 2.5 ml of triton B in two portions over a period of 5 min. Heating at 140° was continued for 45 min., the mixture cooled and diluted with 100 ml 95% ethanol. The crude red-purple solid was filtered, washed with ethanol, air dried and chromatographed on neutral alumina using 9:1 toluene ether as the eluent to yield 2.6 g (65%); m.p. 259-260° (DSC).

Anal. Calcd for  $\text{C}_{51}\text{H}_{33}\text{O}_2\text{N}$ : C, 88.54; H, 4.81; N, 2.02.

Found: C, 88.44; H, 4.85; N, 1.94.

j. Preparation of polypyridine 44

A mixture of 0.69177 g (1.00 mmol) of the biscyclopentadienone 43, 0.12615 (0.100 mmol) of freshly sublimed *p*-diethynylbenzene and 5 ml of chlorobenzene was placed in a 50-ml polymerization tube. The contents of the tube were degassed by several freeze-thaw cycles in liquid  $\text{N}_2$  temperature and then sealed under vacuum. Approximately 300 ml of xylene was added to a Parr pressure reactor, the polymerization tube placed inside, and the reactor was closed and heated at 150° for 18 hr. The temperature was then increased to 230° and the heating continued for an additional 48 hr. After the reaction

had cooled to room temperature, the tube was opened and the resulting polymer dissolved in sym-tetrachloroethane. The polymer was precipitated in petroleum ether, air dried, and stirred with a 5% solution of KOH in absolute ethanol. (The polymer picked up a small amount of hydrogen chloride from the tetrachloroethane.) The polypyridine 44, which was obtained in nearly quantitative yield, was dried under vacuum at 150° for 18 hr:  $n_{inh} = 0.41$  (0.250 g/dl in pyridine at 30°).

The hydrochloride salt of polymer 43 was prepared by stirring the polymer in sym-tetrachloroethane containing a small amount of anhydrous HCl. The solution was dried at 110° for 18 hr:  $n_{inh} = 0.63$  (0.250 g/dl in sym-tetrachloroethane at 30°).

k. 2,6-Diacetylpyridine dihydrazone (46)

A mixture of 5.10 g (0.031 mol) of 2,6-diacetylpyridine, 13 ml (0.25 mol) of 64% aqueous hydrazine, 37.5 ml triethylamine, and 100 ml of ethanol was heated at reflux for 2 hr. The reaction mixture was cooled in ice to yield 5.4 g (91% of white crystals: m.p. 194-195°;  $ir(KBr) 3355\text{ cm}^{-1}$  (s, N-H).

l. Attempted preparation of 2,6-di( $\alpha$ -iodoethenyl)pyridine (47)

A mixture of 10.0 g (0.061 mol) of 2,6-diacetylpyridine dihydrazone, 800 ml tetrahydrofuran and 446 ml of triethylamine under  $N_2$  was treated dropwise with a solution of 65.4 g of iodine (0.26 mol as  $I_2$ ) in 180 ml tetrahydrofuran. When approximately one-half of the solution had been added, a precipitate of triethylammonium iodide formed. After the addition was complete, the reaction mixture was allowed to stir an additional 1 hr at room temperature. The reaction mixture was then filtered and the filtrate concentrated under reduced pressure. The residue was dissolved in methylene chloride, washed with 2N HCl, 5% sodium thiosulfate, and dried over anhydrous  $MgSO_4$ . The resulting black oil could not be crystallized or distilled under vacuum.

m. (p-Bromophenylethynyl)trimethylsilane (49)

The compound was prepared from p-bromoacetophenone by the known procedure<sup>18</sup>: m.p. 60-62° (lit.<sup>18</sup> 62°).

n. (p-Formylphenylethynyl)trimethylsilane (50)

A solution of 15.0 g (0.063 mol) of (p-bromophenylethynyl)-trimethylsilane in 100 ml THF was refluxed 2 hr with 1.6 g (0.066 g atm) of magnesium to form the Grignard reagent. To the reaction mixture was added dropwise 4.61 g (0.063 mol) of dry DMF, and the resulting solution allowed to stir 3 hr at room temperature. The product was hydrolyzed with saturated  $NH_4Cl$  solution and the layers separated. The aqueous layer was washed twice with two 100 ml portions

of ether. The extracts were combined with the original THF layer and dried over  $\text{MgSO}_4$ . The THF-ether was removed under reduced pressure to yield an oil which solidified upon addition of methanol and cooling: ir (KBr) 2190 (s,  $\text{C}\equiv\text{C}$ ) and  $1720\text{ cm}^{-1}$  (s,  $\text{C=O}$ ).

o. Attempted benzoin condensation of (p-formylphenylethynyl)trimethylsilane (50)

A solution of 8.0 g (39.5 mmol) of compound 50 and 2.0 g (30.0 mmol) KCN in 25 ml of 95% ethanol was heated to reflux for 1.5 hr. The solution was cooled and the ethanol was removed under reduced pressure. The oily residue could not be purified.

4. Synthesis and Modification of Phenylated Polyimides

a. General procedure for the polymerization of phenylated dianhydrides 54a and b

In a dry, 25 ml, 3-necked flask equipped with a magnetic stirring bar, a nitrogen inlet, a short-path distillation apparatus and a stopper was placed 0.544 mmol of 1,3-bis(3-aminophenoxy)benzene, 3 ml of m-cresol, and 0.05 g of isoquinoline. After the diamine had dissolved, 0.544 mmol of the dianhydride was added in several portions over 1 hr. The final portion of dianhydride was dissolved in 1 ml of m-cresol, and the solution added to the reaction mixture. The mixture was then stirred for 1 hr at room temperature to yield a viscous, bright-yellow polyamic acid solution. The stopper was replaced by an addition funnel, and the temperature of the flask was increased until distillation commenced. The volume of the solution was maintained at approximately 4 ml by continually replacing the distillate with m-cresol containing 0.025 g/ml of isoquinoline. The distillation-addition cycle was carried out for 3 hr. After the viscous solution was allowed to cool, it was diluted with 15 ml of chloroform and slowly added to 300 ml of vigorously stirred absolute ethanol. The polymer that precipitated was reprecipitated from chloroform with absolute ethanol, collected, and air dried to afford a 95% yield of product. The white polymer was then heat treated to insure complete conversion of the intermediate polyamic acid to the polyimide. A film of the polymer was cast from a 5% chloroform solution on the bottom of a 50-ml round-bottom flask by slowly removing the solvent under reduced pressure. The film was heated under reduced pressure at  $250^\circ$  for 4 hr. The heat-treated polymer was precipitated from chloroform with absolute ethanol, collected and dried under vacuum at  $153^\circ$  for 48 hr.

b. Phenylated dianhydride 57

A mixture of 0.8 g (0.91 mmol) of the biscyclopentadienone 10, 0.1795 g (1.83 mmol) of maleic anhydride, and 5 ml of bromobenzene was placed in a 15 ml, round-bottomed flask and heated at reflux for 3 hr. The reaction mixture was allowed to cool, and a solution of 0.5 ml of bromine in 1.0 ml of bromobenzene was slowly added. The mixture was refluxed for 3 hr with considerable evolution of HBr. The solution was cooled slightly and then slowly added to 300 ml of petroleum ether (bp 60-110°C). The precipitate that formed was collected by filtration, recrystallized twice from bromobenzene and dried under vacuum at 153° for 24 hr to yield 0.58 g (63%) of off-white product: mp 383° (DSC); ir (KBr) 1840, 1780  $\text{cm}^{-1}$  (anhydride).

Anal. Calcd for  $\text{C}_{88}\text{H}_{54}\text{N}_2\text{O}_8$ : C, 83.39; H, 4.29; N, 2.21.

Found: C, 83.26; H, 4.07; N, 1.98.

c. Phenylated polyimide (58)

In a dry, 25-ml, 3-necked flask equipped with a magnetic stirring bar, a nitrogen inlet, a short-path distillation apparatus and a stopper were placed 0.1156 g (0.396 mmol) of 1,3-bis(3-aminophenoxy)benzene, 3 ml of m-cresol, and 0.05 g of isoquinoline. After the diamine had dissolved, 0.4000 g (0.396 mmol) of dianhydride was added in several portions over 1 hr. The final portion of dianhydride was added as a suspension in 1 ml of m-cresol. The dianhydride did not dissolve after 2 hr of stirring at room temperature. The temperature of the mixture was then slowly raised to 150°. During this time, the dianhydride dissolved, and the solution became bright yellow. After heating at 150° for 1 hr the temperature of the flask was increased until distillation commenced (250-270°). The volume of the solution was maintained at approximately 4 ml by continually replacing the distillate with m-cresol containing 0.025 g/ml of isoquinoline. The distillation-addition was continued for 3 hr. After the viscous solution was allowed to cool, it was diluted with 15 ml of chloroform and slowly added to 300 ml of vigorously stirred absolute ethanol. The polymer that precipitated was reprecipitated from chloroform with absolute ethanol, collected, and air dried to yield 0.45 g (90%) of product. Approximately one-half of the fibrous material was placed in a round-bottomed flask and heated

under vacuum. As the temperature neared 250°, the polymer began to flow and form a thin film on the flask. The temperature was increased to 300°, and the heating continued for 2.5 hr. The heat treated polymer was precipitated from chloroform with absolute ethanol, collected, and dried under vacuum at 153° for 24 hr:  $n_{inh} = 1.00$  (0.250 g/dl in sym-tetrachloroethane at 30°).

d. 3,5-Dinitroacetophenone (60)

Treatment of 3,5-dinitrobenzoyl chloride with diethyl malonate followed by decarboxylation as described<sup>20</sup> yielded 3,5-dinitroacetophenone: mp 80-81° (lit.<sup>20</sup> 80-81°).

e. 3,5-Dinitro(1-chloropropen-3-yl)benzene

The following procedure is a modification of that described.<sup>29</sup> Phosphorus oxychloride (3.4 ml, 0.035 mol) was slowly added to 4.2 ml (0.05 mol) of DMF stirred at room temperature to afford a dark red solution. A solution of 5.0 g (0.029 mol) of 3,5-dinitroacetophenone in 10 ml of DMF was then slowly added to the DMF/ $POCl_3$  complex. After the addition was complete, the reaction mixture was heated at 110° for 30 min and then allowed to stand at room temperature overnight. The mixture was poured with stirring into 70 ml of ice water to afford a dark red gum which crystallized on stirring with hot ethanol: ir ( $C_6H_6$ ) 2900 (CHO), 1750 (C=O), and 1550, 1370  $cm^{-1}$  ( $NO_2$ ). Attempts to recrystallize the dark red solid were unsuccessful.

f. Attempted preparation of 3,5-dinitrophenylacetylene (61)

To a solution of 4.02 g (0.1 mol) of sodium hydroxide in 40 ml of water heated to reflux was slowly added a solution of 10.0 g (0.039 mol) of crude 3,5-dinitro(1-chloropropen-3-yl)benzene in 40 ml of dioxane. After the addition was complete, the reaction mixture was heated at reflux for 1 hr. Approximately one-half of the solvent was removed under reduced pressure, and the residue was poured into 500 ml of ice water. Extraction of the aqueous solution with benzene afforded a yellow solid that showed no acetylenic infrared absorptions.

g. 3,5-Dinitroacetophenone hydrazone (63)

A mixture of 6.4 g (0.03 mol) of 3,5-dinitroacetophenone, 8 ml 64% aqueous hydrazine, 38 ml triethylamine, and 100 ml of ethanol was refluxed for 4 hr. The reaction mixture was then cooled and poured

with stirring into 500 ml of ice-cold water. The resulting precipitate was filtered, washed with water, and air dried to yield 4.0 g (60%) of the hydrazone: mp 116-118°; ir (KBr) 3350  $\text{cm}^{-1}$  (m, N-H).

h. Attempted preparation of 3,5-dinitro- $\alpha$ -iodostyrene (64)

A solution of 4.0 g (0.019 mol) of 3,5-dinitroacetophenone hydrazone, 500 ml tetrahydrofuran, and 250 ml of triethylamine was treated dropwise, under nitrogen, with a solution of 18.0 g of iodine (0.07 mol as  $\text{I}_2$ ) in 50 ml tetrahydrofuran. After stirring for 1 hr, the triethylammonium iodide that formed during the course of the reaction was filtered and washed with tetrahydrofuran. The combined filtrates were concentrated under reduced pressure, dissolved in methylene chloride, washed with 2N hydrochloric acid and 5% sodium thiosulfate solution, and dried (anh  $\text{MgSO}_4$ ). Removal of the solvent yielded 1.0 g of an oily product that could not be identified.

i. 3,5-Dinitroaniline (65)

Treatment of 3,5-dinitrobenzoyl chloride with sodium azide according to the known procedure<sup>21</sup> afforded 3,5-dinitrobenzoyl azide. This azide was then heated in sulfuric acid to yield 3,5-dinitroaniline: mp 103-106° (lit.<sup>21</sup> 106-107°).

j. 3,5-Dinitrofluorobenzene (66)

Diazotization of 65 followed by treatment with sodium fluoroborate as described gave a 5% yield of 3,5-dinitrofluorobenzene: mp 41-42° (lit.<sup>21</sup> 42-43°).

k. 3,5-Dinitrobromobenzene (73)

Treatment of 3,5-dinitrobenzoic acid with silver nitrate as described<sup>22</sup> afforded the corresponding silver salt. The reaction of this salt with  $\text{Br}_2$  gave a 58% yield of compound 73: mp 76-78° (lit.<sup>22</sup> 77-78°).

l. p-Hydroxyacetophenone Tosylate (67)

The reaction of p-toluene sulfonyl chloride with p-hydroxyacetophenone according to the described procedure<sup>29</sup> afforded the tosylate of p-hydroxyacetophenone: mp 73-74° (lit.<sup>30</sup> 72-73°).

m. p-Toluene sulfonate ester of 4-hydroxy(1-chloropropen-3-yl) benzene

The reaction of a  $\text{DMF-POCl}_3$  complex with p-hydroxyacetophenone

tosylate according to the described procedure<sup>29</sup> afforded this intermediate, mp 127-129° (acetone): ir (KBr) 2880 (CH<sub>3</sub>) and 1680 cm<sup>-1</sup> (C=O).

Anal. Calcd for C<sub>16</sub>H<sub>13</sub>ClO<sub>3</sub>S: C, 57.05; H, 3.88; Cl, 10.52; S, 9.52.

Found: C, 56.87; H, 3.95; Cl, 10.69; S, 9.51.

n. 4-Ethynylphenyl-p-toluene sulfonate (68)

Treatment of the previous compound with sodium hydroxide as described<sup>29</sup> provided 4-ethynylphenyl-p-toluene sulfonate, mp 84-85° (CH<sub>2</sub>Cl<sub>2</sub>): ir (KBr) 3320 cm<sup>-1</sup> (≡C-H); nmr (CDCl<sub>3</sub>) δ 2.4 (s, 3H), 3.05 (s, 1H), and 6.8-7.8 ppm (m, 8H).

Anal. Calcd for C<sub>15</sub>H<sub>12</sub>O<sub>3</sub>S: C, 66.15; H, 4.44; S, 11.77.

Found: C, 66.19; H, 4.67; S, 12.00.

o. Sodium 4-ethynylphenoxide (69)

To a stirred suspension of 2.0 g (0.035 mol) of sodium methoxide in 100 ml of benzene under nitrogen was slowly added a solution of 4.1 g (0.035 mol) of p-hydroxyphenylacetylene in 50 ml of benzene. A green precipitate formed immediately. After the addition was complete, the mixture was stirred for 15 min at room temperature. The solvent was then removed under reduced pressure, and the residue stored in an ice bath under nitrogen.

p. Attempted preparation of 4-(3,5-dinitrophenoxyphenylacetylene (70))<sup>31</sup>

Pyridine (70 ml) was added to the residue described above, and the resulting solution heated at reflux under nitrogen for 5 min. After the heating was discontinued, 17.3 g (0.070 mol) of 1-bromo-3,5-dinitrobenzene and 1 g freshly prepared cuprous chloride were added. The reaction mixture was heated at reflux under nitrogen for 9 hr, cooled in an ice bath, and acidified with hydrochloric acid. The mixture was then extracted with three 50-ml portions of ether. After the ether extract was washed with 5% sodium hydroxide and 5% sodium chloride, it was dried over anhydrous sodium sulfate. The ether was removed under reduced pressure to afford the unreacted starting material.

q. Preparation of 4-(2,4-dinitrophenoxy)phenylacetylene (75)

Procedure 1

A mixture of 7.5 g (27.5 mmol) of the tosylate of 4-ethynylphenol and a solution made by dissolving 4.6 g (83 mmol) of potassium



hydroxide in 50 ml of absolute methanol was heated at reflux for 1.5 hr under nitrogen. The solvent was removed under reduced pressure and 50 ml of benzene was added. The benzene was then distilled azeotropically to remove any water present. The resulting solid was dissolved in 25 ml of dry DMF and cooled in a dry ice-acetone bath to  $-30^{\circ}$ . A solution of 5.1 g (23.4 mmol) of 2,4-dinitrofluorobenzene in 30 ml of DMF at  $-30^{\circ}$  was added under nitrogen to the solid. The mixture was stirred at room temperature for 1 hr, heated to reflux for an additional 1 hr, cooled, and poured with vigorous stirring into 500 ml of an ice cold solution of 5% sodium hydroxide. A black tar resulted that could not be further purified.

#### Procedure 2

The procedure was followed as described above except pyridine was used as the solvent, and the following changes were made in the work-up of the reaction mixture. The pyridine was removed under reduced pressure at the end of the reflux period. The resulting black tarry product was extracted with chloroform and the organic layer washed with 5% hydrochloric acid, 5% sodium hydroxide, and finally with water. The solution was dried over anhydrous sodium sulfate and reduced in volume under reduced pressure to yield an unidentifiable black tarry product.

#### Procedure 3

The procedure was the the same as described in 1 except the reaction was carried out at room temperature for 18 hr. The reaction mixture was then poured into cold 5% sodium hydroxide to give a dark yellow solid. Recrystallization from ethanol gave 4.0 g of a compound melting at  $73-74^{\circ}$ . The infrared spectrum shows an acetylenic C-H stretch at  $3300\text{ cm}^{-1}$  but nmr analysis shows the structure of the compound to be inconsistent with that of 2,4-dinitro-4'-ethynyldiphenyl ether.

#### Procedure 4

A mixture formed by adding 7.5 g (27.5 mmol) of the tosylate of 4-ethynylphenol to a solution containing 4.6 g (83 mmol) of potassium hydroxide in 50 ml of absolute methanol was heated at reflux for 1.5 hr under nitrogen. The solvent was removed under reduced pressure, and 150 ml of water added to the resulting solid. The aqueous mixture

was extracted twice with 50 ml-portions of methylene chloride to remove any unreacted starting material. The aqueous layer was cooled and acidified with 1N sulfuric acid. The acidified solution was extracted three times with 50 ml-portions of methylene chloride. The combined methylene chloride extracts were washed with 50 ml of water, concentrated to 15 ml, and chromatographed on dry silica gel with 350 ml of methylene chloride. The solvent was removed under reduced pressure to yield 3.3 g of 4-ethynylphenol. The phenol was dissolved in 50 ml of benzene and added dropwise under nitrogen to a rapidly stirred suspension of 1.5 g (28.0 mmol) of sodium methoxide in 50 ml of benzene. The reaction mixture was stirred for 15 min, the solvent removed under reduced pressure, and 50 ml of dry DMF added to the resulting solid. A solution containing 5.1 g (28.0 mmol) of 2,4-dinitrofluorobenzene in 50 ml of dry DMF at  $-30^{\circ}$  was then added dropwise under nitrogen to the suspension of sodium 4-ethynylphenolate in DMF, which was cooled in an ice bath. The reaction mixture was allowed to warm to room temperature and stirred for 50 hr. The reaction mixture was poured slowly into 800 ml of a 1% ice cold solution of sodium hydroxide. The resulting yellow solid was filtered, washed with cold water, and recrystallized from ethanol to yield 6.0 g (77%) of 4-(2,4-dinitrophenoxy)phenylacetylene: mp  $124-125^{\circ}$ ; ir (melt on salt plates)  $3290$  (s,  $\equiv\text{C-H}$ ),  $1530$ ,  $1350\text{ cm}^{-1}$  (s,  $\text{NO}_2$ ); nmr ( $\text{CDCl}_3$ )  $\delta$  3.08 (s, 1H,  $\equiv\text{C-H}$ ), 7.3 (s, 4H,  $\text{p-C}_6\text{H}_4$ ) and 8.5 ppm (m, 3H, 1,2,4-trisubstituted aromatic ring).

Anal. Calcd for  $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_5$ : C, 59.15; H, 2.83; N, 9.85.

Found: C, 59.18; H, 2.79; N, 10.17.

r. Attempted reduction of 4-(2,4-dinitrophenoxy)phenylacetylene (75)

Procedure 1 <sup>32</sup>

A solution of 6.53 g (23.0 mmol) of 75 in 25 ml of THF was added dropwise to a suspension of 6.07 g (46.0 mmol) of  $\text{NaBH}_2\text{S}_3$  in 40 ml of THF under nitrogen. The reaction mixture was stirred and heated at reflux under nitrogen for 24 hr. After the solvent was removed under reduced pressure, the residue was hydrolyzed with 10% hydrochloric acid in the presence of 25 ml of ether. The precipitated

sulfur was filtered off, and the filtrate washed repeatedly with ethyl ether. The aqueous fraction was neutralized with 20% sodium hydroxide in the presence of 50 ml of ether. The aqueous layer was extracted with ether. The ether extracts were combined, washed with a saturated salt solution, and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure to yield a brown oil that showed no acetylenic infrared absorptions:  $\text{ir (neat)}$  3450 and 3350  $\text{cm}^{-1}$  (N-H).

#### Procedure 2<sup>29</sup>

To a rapidly stirred solution of 41 g (230 mmol) of sodium hydrosulfite and 32 g (230 mmol) of potassium carbonate in 250 ml of water was slowly added a solution of 6.7 g (23.4 mmol) of compound 75 in 50 ml of dioxane. The reaction mixture became hot as the solution changed from yellow to white. After the mixture was stirred for 30 min the dioxane was removed under reduced pressure. The aqueous solution was repeatedly extracted with methylene chloride. The solvent was removed under reduced pressure to afford 0.2 g of brown oil that could not be further purified:  $\text{ir (neat)}$  3450, 3350 (N-H), 3280 and 2100  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C-H}$ ).

The following modifications of the above procedure were carried out in attempts to increase the yield:

1. Methanol, THF, DMF, DMAC, and ethanol were used in place of dioxane.
2. No organic solvent was used.
3. Ammonium hydroxide and sodium hydroxide were used in place of potassium carbonate.<sup>33</sup>
4. Solid sodium hydrosulfite was added in portions to a mixture of the dinitro compound, base, water, and the organic solvent.<sup>33</sup>
5. A molar ratio of compound 75 to base of 1:15 was used.
6. The reaction was carried out under nitrogen.
7. After removal of the organic solvent, the aqueous solution was made strongly acidic with hydrochloric acid and concentrated to 50 ml.
8. Extraction was carried out with ethyl acetate.

In all modifications, the reaction mixture became hot indicating

reduction was taking place. However, only very small amounts of crude product could be isolated.

Procedure 3 <sup>34</sup>

To a mixture of 160 g (1.052 mol) ferrous sulfate, 35 ml ethanol, 8.0 g (0.028 mol) compound 75, and 260 ml of water that had been heated at reflux under nitrogen for 2 hr was slowly added 55 ml of concentrated ammonium hydroxide. The reaction mixture was heated at reflux overnight, an additional 30 ml of ammonium hydroxide was added, and the mixture allowed to cool for one hr. The solution was filtered, and the precipitated iron hydroxides washed with ether. After the filtrate was extracted several times with ether, the extracts were combined and dried over anhydrous potassium carbonate. However, no product was isolated when the ether was removed under reduced pressure.

Procedure 4 <sup>35</sup>

A mixture of 7.2 g (0.025 mol) compound 75, 120 g (1.83 mol) of zinc dust, 4 g calcium chloride in 6 ml of water, and 200 ml of 78% ethanol was heated at reflux for 8 hr under nitrogen. The hot solution was filtered, and the sludge of zinc dust was washed with hot ethanol. The filtrate was reduced to low volume under reduced pressure, acidified with 10% hydrochloric acid, washed with ether, neutralized with 10% sodium hydroxide, and extracted several times with ether. The combined ether extracts were washed with a saturated solution of sodium chloride and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure to afford 3.2 g of a dark brown oil. The infrared indicated that the nitro groups had been reduced, however, the spectrum did not show any acetylenic absorptions:  $\text{ir (neat) } 3450 \text{ and } 3350 \text{ cm}^{-1} \text{ (N-H)}$ .

Procedure 5 <sup>36</sup>

A mixture of 1 g (3 mmol) of compound 75, 35 ml of ethyl acetate, 1.7 g (28 mmol) of Raney nickel (W2), 7 ml of water, and 35 ml of ethanol was shaken under 15 psi of hydrogen at room temperature for 2 hr. The reaction mixture was reduced to low volume under reduced pressure. The filtrate was acidified with 10% hydrochloric acid, washed with ether, neutralized with 20% sodium hydroxide, and extracted several times with ether. The ether was removed under reduced

pressure to afford a brown oil which did not show acetylenic infrared absorptions: ir (neat) 3450 and 3350  $\text{cm}^{-1}$  (N-H).

s. 4-(2,4-Dinitrophenoxy)acetophenone hydrazone (78)

A mixture of 86 g (0.28 mol) of 4-(2,4-dinitrophenoxy)acetophenone, 70 ml 64% aqueous hydrazine, 338 ml of triethylamine, and 1 l of ethanol was refluxed for 5 hr. The solution was concentrated to approximately 300 ml, cooled, and filtered. The product was washed with a minimum volume of ice-cold ethanol and air dried to yield 53 g (60%) of bright yellow crystals: mp 210-211°; ir (KBr) 3350  $\text{cm}^{-1}$  (m, N-H).

t. Attempted preparation of 4-(2,4-dinitrophenoxy)- $\alpha$ -iodostyrene (79)

Treatment of compound 78 with iodine under the conditions described for compound 5 resulted in 4% yield of a crude brown-black oil.

u. 3,5-Dinitroiodobenzene (80)

Compound 80 was synthesized by the iodination of m-dinitrobenzene according to the known procedure<sup>24</sup> to afford a 55% yield of yellow crystals: mp 99-100° (lit.<sup>24</sup> 99.5-100.5°).

v. 3,5-Dinitrodiphenylacetylene (82)

A mixture of 25.0 g (0.085 mol) of 3,5-dinitroiodobenzene, 13.99 g (0.085 mol) copperphenylacetylide, and 300 ml of pyridine was refluxed for 24 hr under nitrogen. Most of the pyridine was then removed under reduced pressure and the residue diluted with water (300 ml). The mixture was extracted 4 times with chloroform and the combined extracts were washed successively, 4 times each, with dilute hydrochloric acid, 5% sodium carbonate solution, and water and dried over anhydrous magnesium sulfate. The solution was reduced to low volume and the residue chromatographed on silica gel using methylene chloride. Evaporation of the solvent yielded 10 g (40%) of brown crystals. Recrystallization from absolute ethanol afforded brown needles: mp 166-168°; ir (KBr) 2221  $\text{cm}^{-1}$  (m,  $\text{C}\equiv\text{C}$ ).

w. Attempted reduction of 3,5-dinitrodiphenylacetylene (82)

Procedure 1

To a rapidly stirred solution of 19.5 g (0.112 mol) of sodium hydrosulfite and 15.5 g (0.112 mol) of potassium carbonate in

120 ml of water was slowly added a solution of 3.0 g (0.112 mol) of compound 82 in 50 ml of dioxane. The solution, which did not undergo a dramatic color change, was stirred for 2 hr and then extracted with methylene chloride. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness. The brown tarry residue was taken up in benzene and precipitated in petroleum ether to afford 0.3 g of a light brown powder, which showed no acetylenic infrared absorptions: mp 104-108°.

The above procedure was repeated with the reaction mixture being heated at reflux under nitrogen for 2 hr. However, identical results were obtained. The procedure was also carried out with DMAC as the solvent to afford a black tar.

#### Procedure 2<sup>29</sup>

To a refluxing solution of 13.4 g (0.089 mol) ferrous sulfate in 184 ml water under nitrogen was slowly added a solution of 1.0 g (0.004 mol) of compound 82 in 100 ml of dioxane. The mixture was stirred 5 min, and 74 ml of 30% ammonium hydroxide was added dropwise. After the dark suspension was heated at reflux for 30 min, an additional 74 ml of ammonium hydroxide was added. The mixture was heated 30 min, cooled, and extracted with chloroform. The solvent was removed under reduced pressure to afford a brown tar, which was taken up in chloroform and precipitated in petroleum ether. The small amount (0.1 g) of yellow product could not be further purified: ir (KBr) 3480, 3380 (N-H) and 2200  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{CH}$ ).

#### Procedure 3

To a refluxing solution of 7.0 g (0.026 mol) of compound 82 and 5 ml of 20% sodium hydroxide in 100 ml of ethanol was slowly added 10 g of zinc dust. After the addition was complete, the mixture was heated at reflux for 1 hr. The mixture was extracted with chloroform, and the combined extracts evaporated to dryness to yield a brown solid, which showed no acetylenic infrared absorptions.

#### x. 2,4-Dinitroiodobenzene

This compound was prepared according to the known procedure<sup>37</sup>: mp 88-90° (lit.<sup>37</sup> 88.5-90°).

y. 2,4-Dinitrodiphenylacetylene

A mixture of 8.0 g (0.027 mol) of 2,4-dinitroiodobenzene, 4.48 g (0.027 mol) of cuprous phenylacetylide and 110 ml of HMPA was slowly heated under nitrogen to 90°. The resulting brown solution was cooled and added to 2  $\times$  of ice water. The precipitate that formed was extracted with ethanol and recrystallized from petroleum ether to afford 6.8 g (93%) of yellow needles: mp 120-121.5° (lit.<sup>38</sup> 112-114°), ir (KBr) 2200  $\text{cm}^{-1}$  (C $\equiv$ C-H).

z. Attempted reduction of 2,4-dinitrodiphenylacetylene

Procedure 1

Treatment with sodium hydrosulfite as described for compound 75 afforded a 6% yield of a crude yellow solid that could not be purified: ir (KBr) 3480, 3380  $\text{cm}^{-1}$  (N-H) and 2200  $\text{cm}^{-1}$  (C $\equiv$ C-H).

Procedure 2

Treatment with  $\text{NaBH}_2\text{S}_3$  as described for compound 75 produced a dark brown tar that could not be purified.

Procedure 3

To a mixture of 1.4 g (0.005 mol) 2,4-dinitrodiphenylacetylene, 1.37 g (0.021 mol) zinc dust, and 10 ml of acetic acid under nitrogen was slowly added 20 ml of concentrated hydrochloric acid. During the addition the mixture was cooled in a water bath to control the brisk evolution of hydrogen gas. The mixture was then heated at 40° with stirring for 1 hr, cooled and filtered. The filtrate was neutralized with sodium bicarbonate to afford a yellow solid that was collected by filtration, washed with water, and dried. The product was chromatographed on silica gel with ethanol to yield 0.3 g of a yellow solid that displayed a wide melting range: ir (KBr) 3460, 3380 (N-H) and 2200  $\text{cm}^{-1}$  (C $\equiv$ C-H).

aa. 4,4'-Diacetamidobenzil (86)

This compound was prepared from p-acetamidobenzaldehyde according to the known procedure:<sup>25</sup> mp 249-250°.

bb. 3,4-Bis(4-acetamidophenyl)-2,5-diphenylcyclopentadienone (87)

To a suspension of 10.0 g (30.8 mmol) 4,4'-diacetamidobenzil in 150 ml of absolute ethanol was added 6.50 g (30.8 mmol) of diphenylacetone. The reaction mixture was heated to reflux, and 5 ml of a 10%



solution of sodium hydroxide in absolute ethanol was added dropwise. Upon addition of the base, the benzil went into solution, and the reaction mixture turned dark purple. After approximately 5 min, a second 5 ml portion of base was added. The reaction mixture was refluxed an additional 30 min and then cooled in ice. The dark solid that precipitated was collected by filtration and recrystallized from methyl cellosolve to give 6.0 g (40%) of the dark purple product: mp 301-302°.

Anal. Calcd for  $C_{33}H_{26}O_3N_2$ : C, 79.49; H, 5.26; N, 5.62

Found: C, 79.64; H, 5.34; N, 5.70

cc. 4,4''-Bisacetamido-3',6'-diphenyl-4'-(p-ethynylphenyl)-o-terphenyl (88)

A suspension of 6.0 g (12.0 mmol) of 3,4-bis(4-acetamidophenyl)-2,5-diphenylcyclopentadienone and 6.5 g (0.05 mol) of freshly sublimed p-diethynylbenzene in 50 ml diglyme was heated at reflux under nitrogen for 40 min. The resulting light orange solution was cooled and poured into 2 l of hexane. The off-white solid that precipitated was collected by filtration and recrystallized from ethyl acetate (charcoal) to yield 6.3 g (88%): mp 312-14°(dec.); ir (KBr) 1658 (s, C=O), 3285  $cm^{-1}$  (s,  $\equiv$ C-H).

dd. 4,4''-Diamino-3',6'-diphenyl-4'-(p-ethynylphenyl)-o-terphenyl (89)

A suspension of 0.50 g of compound 88 in 25 ml of a potassium hydroxide solution (88 g KOH in 70 ml  $H_2O$ , diluted with 250 ml 95% EtOH) was heated at reflux for 4 hr. The solid appeared to slowly go into solution and then reprecipitate. The suspension was cooled and poured into 600 ml of water. The off-white solid was filtered, air dried, and chromatographed on silica gel using 3:1 chloroform-ethyl acetate. The elution of the column was followed by TLC. The chloroform-ethyl acetate solution was reduced in volume under nitrogen and precipitated with hexane to give 0.60 g (70%): mp 155° dec.; ir (KBr), 3280  $cm^{-1}$  (s,  $\equiv$ C-H).

ee. Polymerization of 4,4'-(oxydi-1,4-phenylene)bis[3,5,6-triphenylphthalic anhydride] (54b) and 4,4''-diamino-3',6'-diphenyl-4'-(p-ethynylphenyl)-o-terphenyl (89)

In a dry, 3-necked flask equipped with a magnetic stirring bar, a nitrogen inlet, a short-path distillation apparatus and a stopper was placed 0.2789 g (0.544 mmol) of the diamine, 3 ml of freshly distilled m-cresol, and 0.05 g of isoquinoline. After the diamine had dissolved to give an orange-red solution, 0.5000 g (0.544 mmole) of dianhydride was added in several portions over 1 hr. The final portion of dianhydride was dissolved in 1 ml of m-cresol, and the solution added to the reaction mixture. The mixture was stirred for 1 hr at room temperature. The viscosity of the solution increased slightly, however, the bright yellow color characteristic of previous polymerizations was not observed until the temperature of the mixture had been increased to 130-150°. The stopper was replaced by an addition funnel, and the temperature of the flask was increased until distillation commenced (220°). The volume of the solution was maintained at approximately 4 ml by continually replacing the distillate with m-cresol containing 0.025 g/ml of isoquinoline. The distillation-addition cycle was carried out for 1.5 hr. After the solution was allowed to cool, it was slowly added to 300 ml of vigorously stirred methanol. The polymer that precipitated was reprecipitated from chloroform with methanol, collected and air dried to afford a 93% yield of product:  $\eta_{inh} = 0.12$  (0.250 g/dl in sym-tetrachloroethane at 30°).

5. Acetylene-Terminated Polyphenylene Oligomers

a. Acetylene terminated polyphenylene oligomers (91a-c)

A solution of 3.12 g (4.0 mmol) of 3,3'-(oxydi-p-phenylene)bis-[2,4,5-triphenylcyclopentadienone] and 2.00 g (16.0 mmol) of p-diethynylbenzene in 35 ml toluene was heated at reflux under nitrogen for 8 hr. The reaction mixture was cooled and added dropwise to 1  $\ell$  of hexane. The resulting white solid that precipitated was collected by filtration, reprecipitated from benzene-hexane and air dried: ir (KBr)  $2200\text{ cm}^{-1}$  ( $\text{C}\equiv\text{C-H}$ )

b. Thermal Crosslinking of Acetylene Terminated Polyphenylene  
Oligomers

A 0.5 g sample of 91 was heated at 250° under N<sub>2</sub> for 3 hr. The resulting light tan solid was completely insoluble in organic solvents and showed no acetylenic infrared absorptions.

APPENDIX  
Infrared Spectra and Thermal Analyses

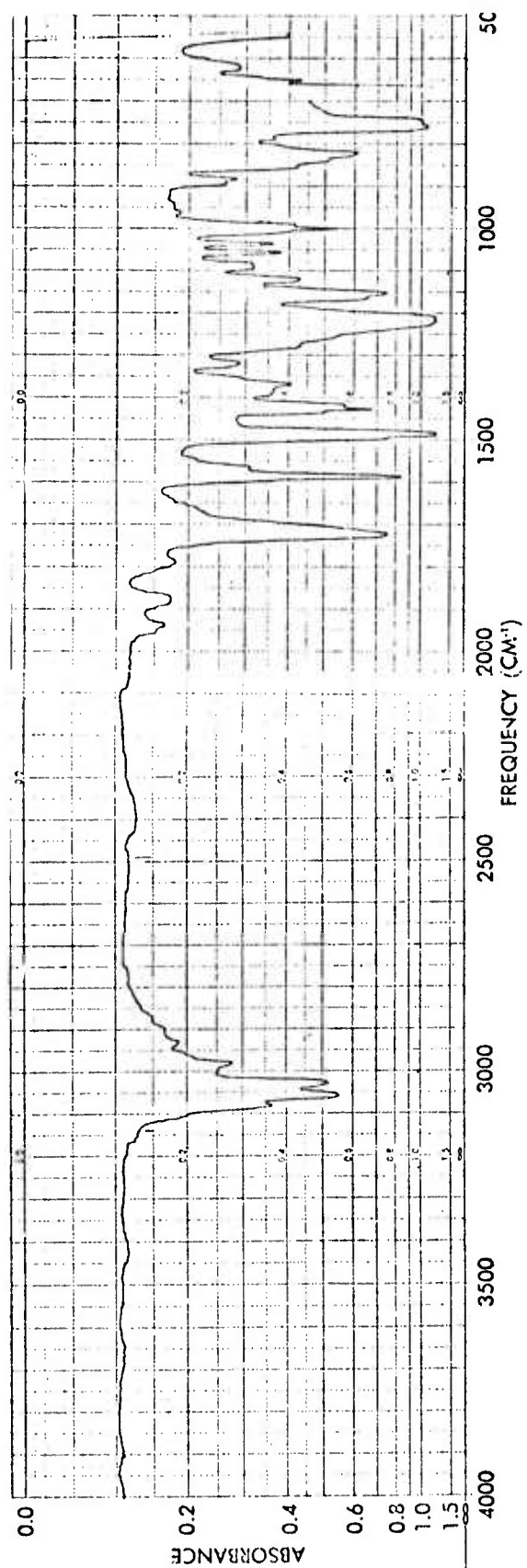


Figure 1. Infrared Spectrum of Polymer 16a.

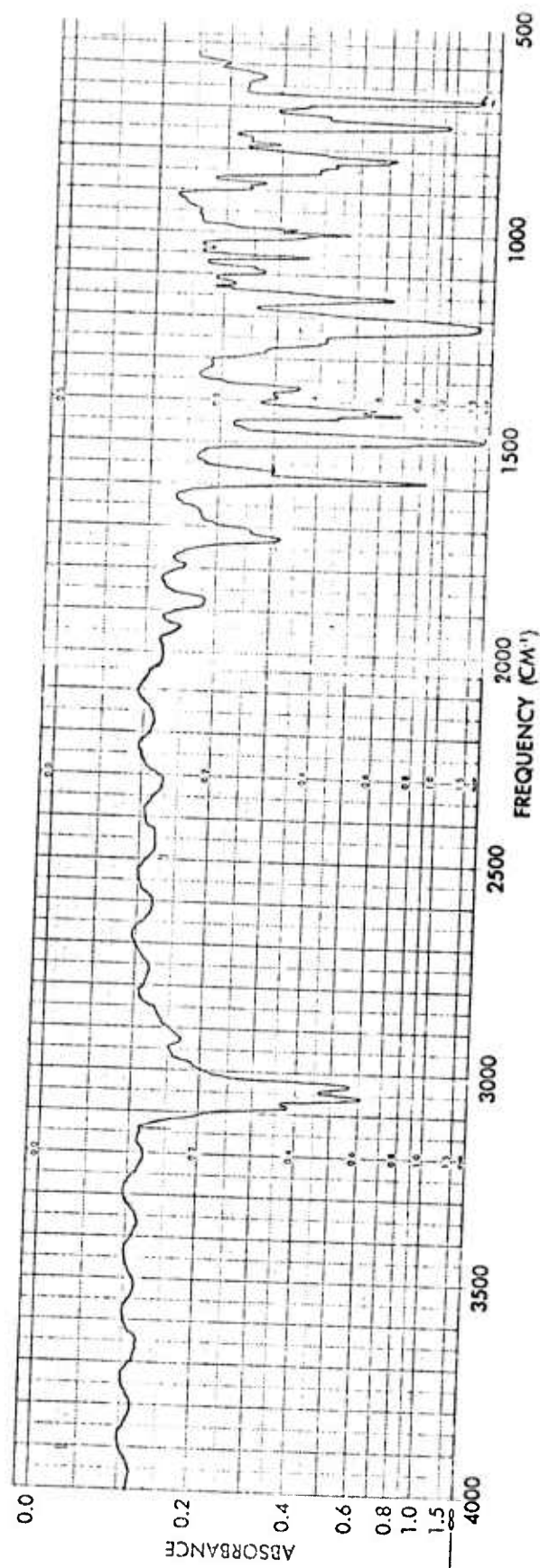


Figure 2. Infrared Spectrum of Polymer 16b.

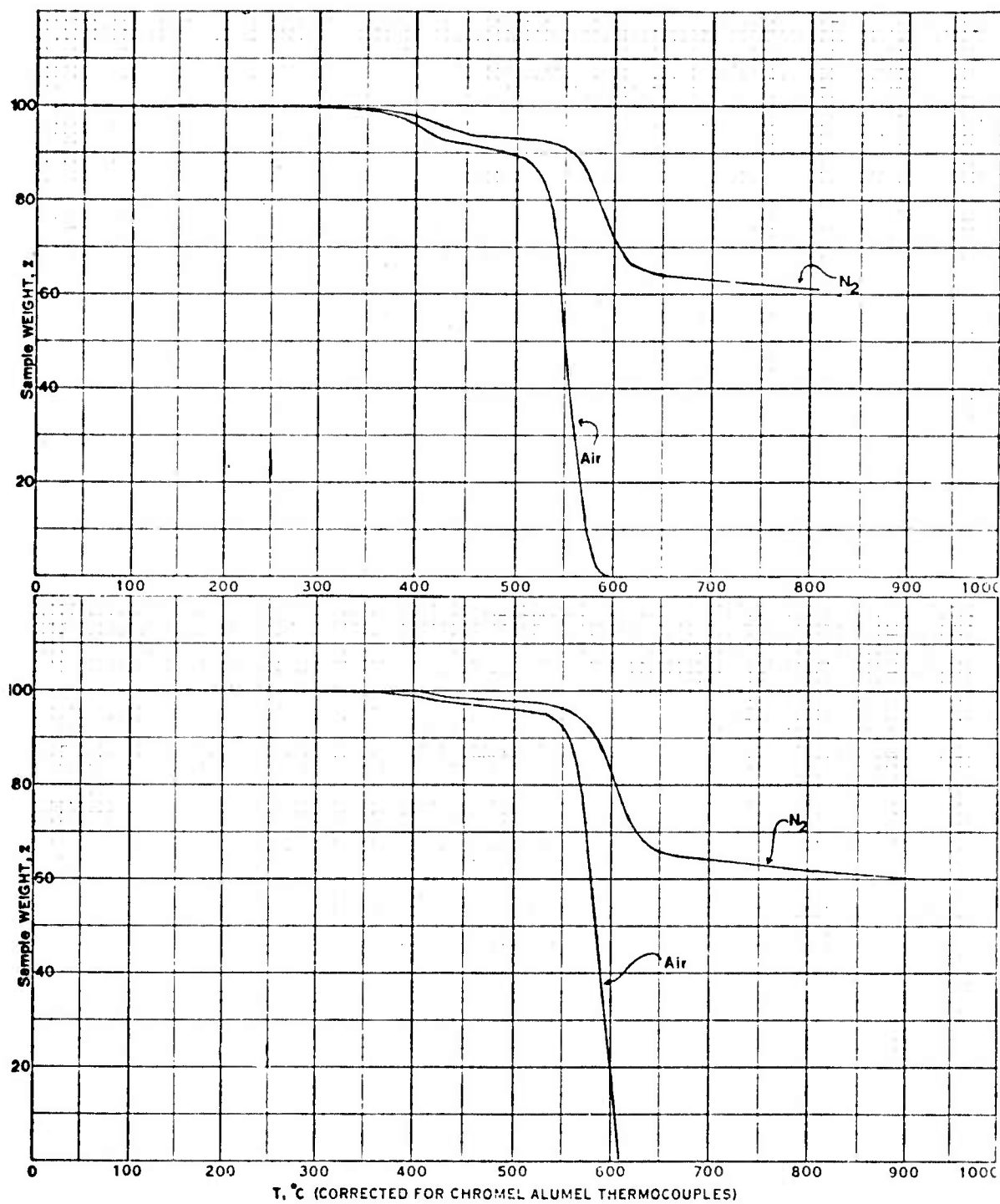


Figure 3. Thermogravimetric Analysis of Polymer 16a and 16b.



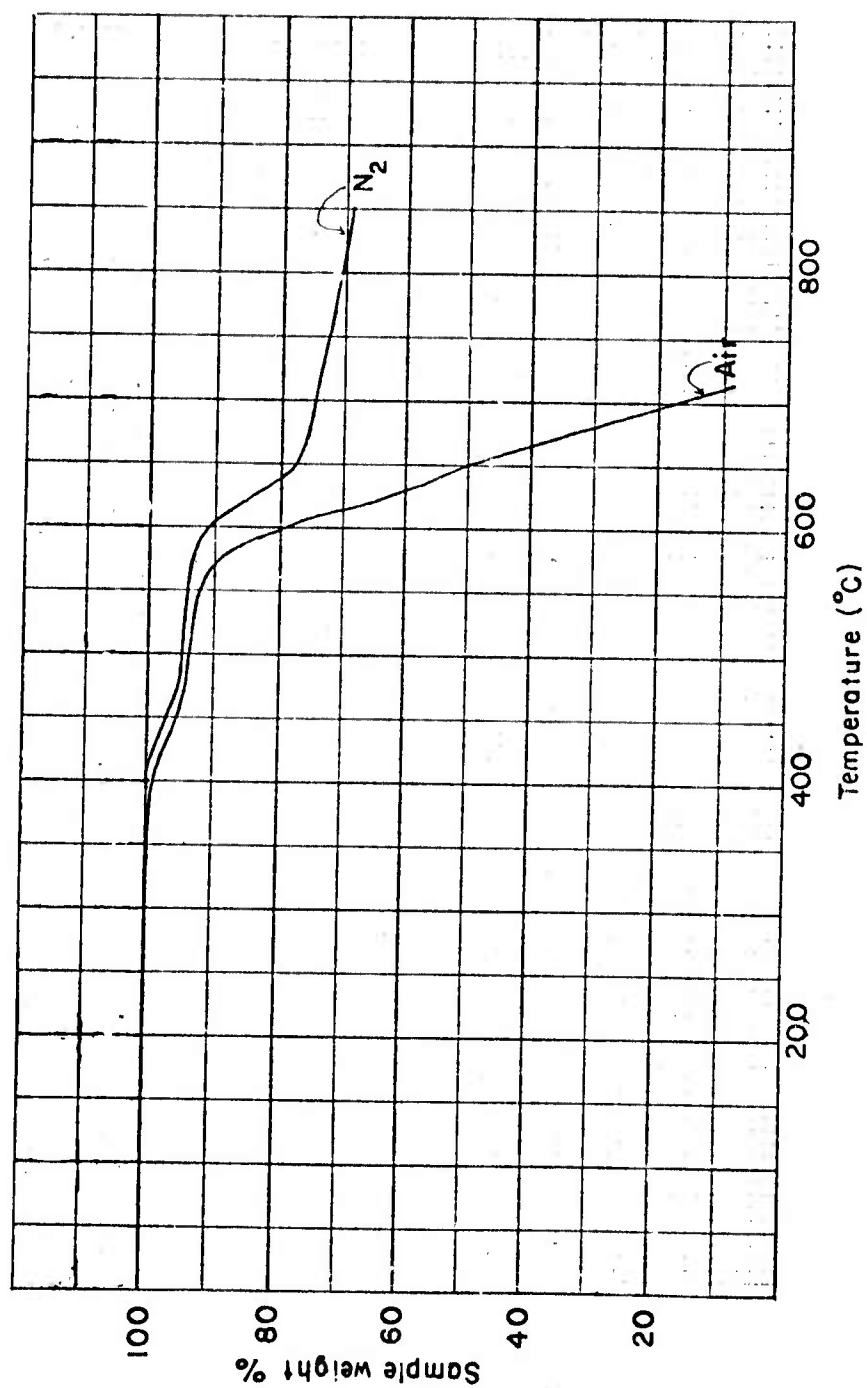


Figure 4. Thermogravimetric Analysis of Polymer 17.

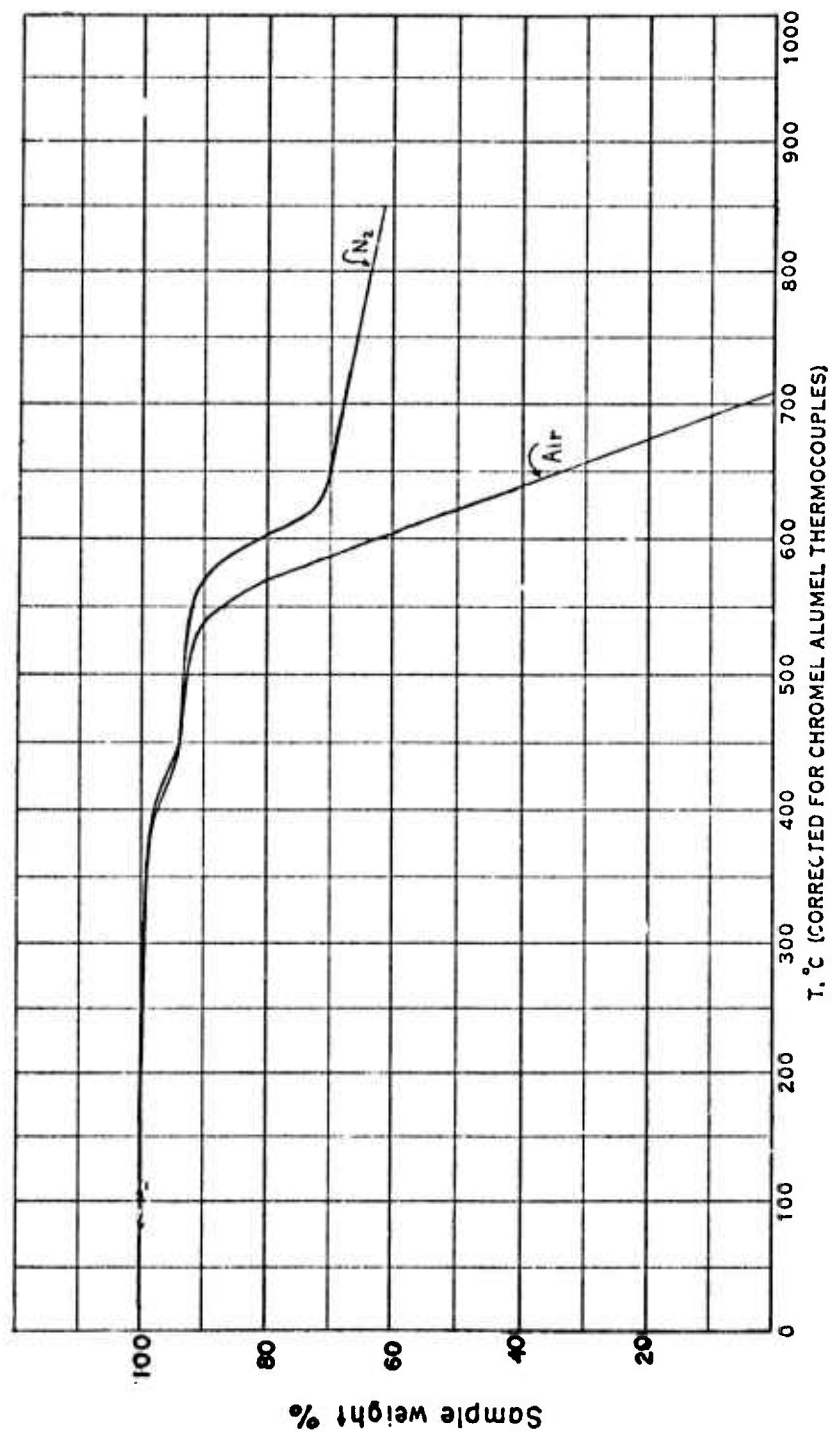


Figure 5. Thermogravimetric Analysis of Polymer 18.

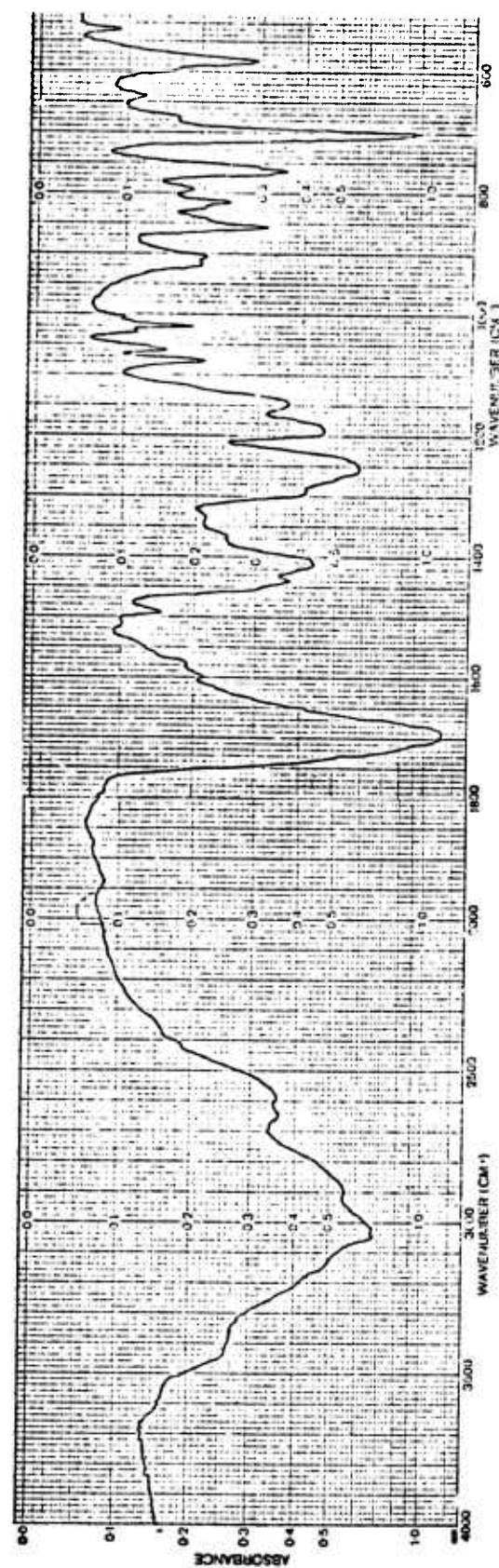


Figure 6. Infrared Spectrum of Compound 23.

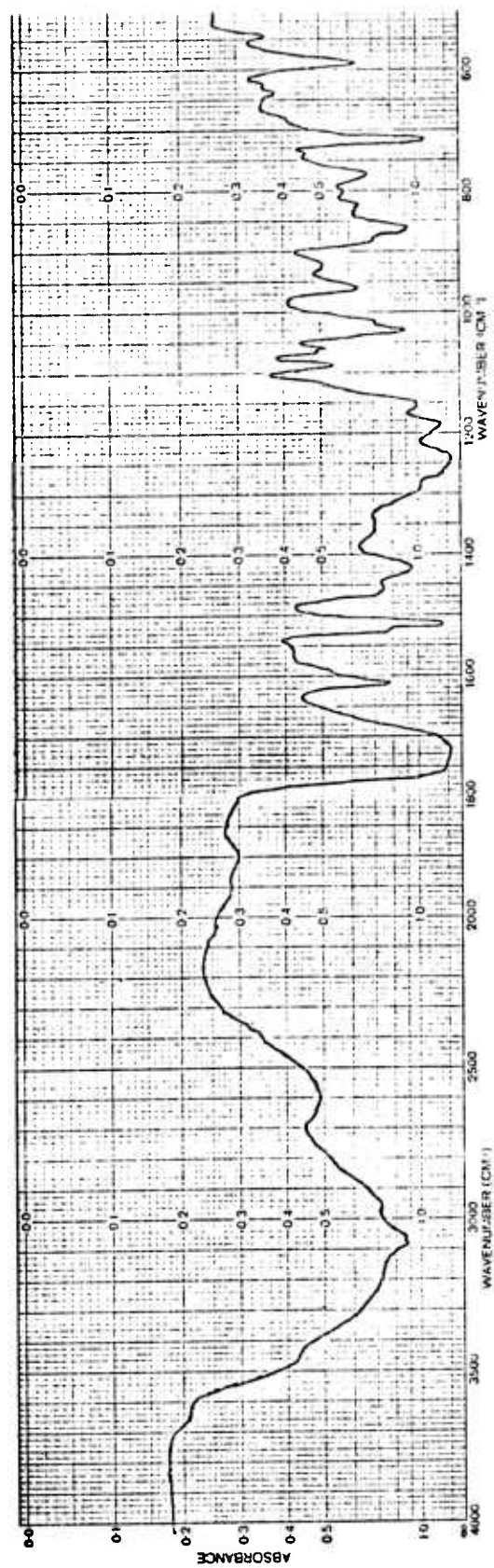


Figure 7. Infrared Spectrum of Polymer 25.

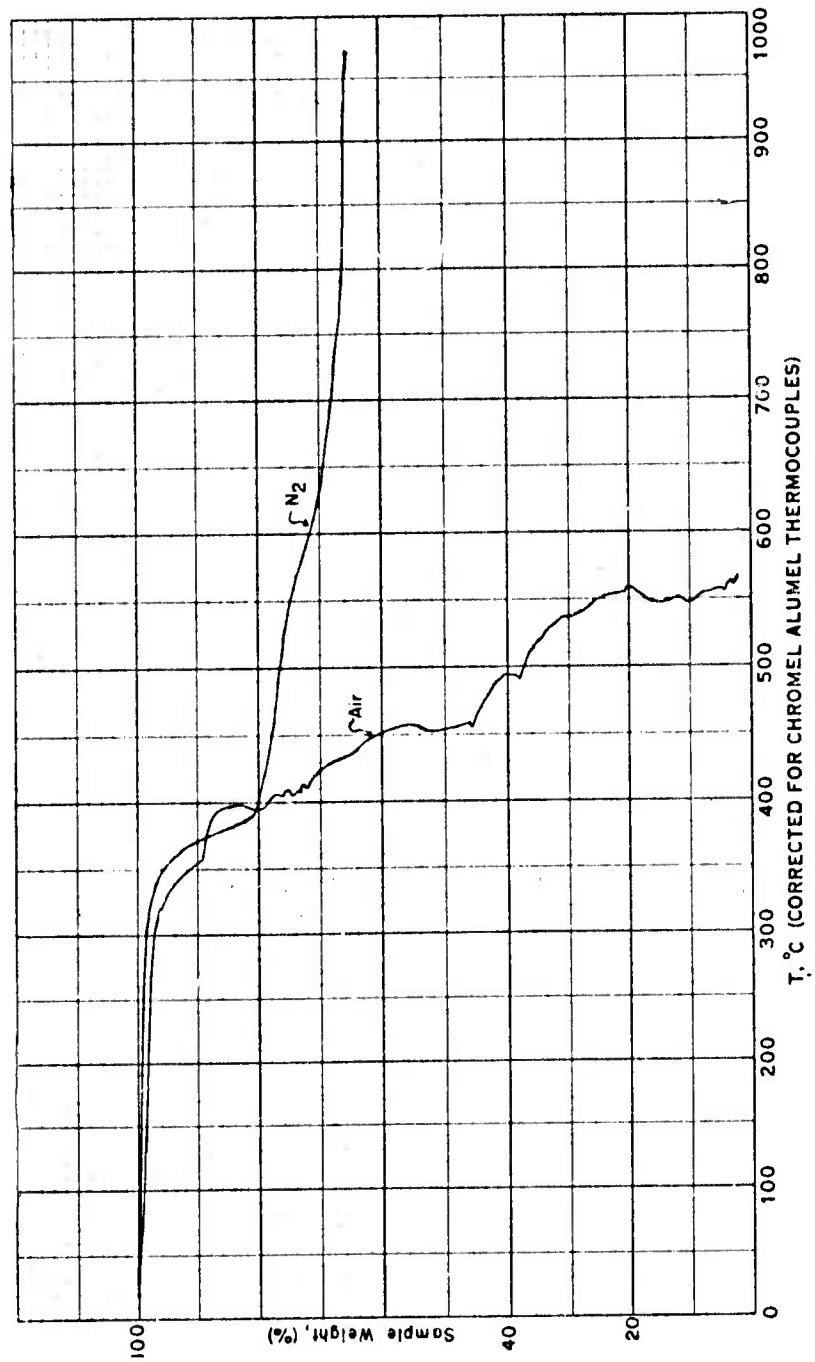


Figure 8. Thermogravimetric Analysis of Polymer 25.

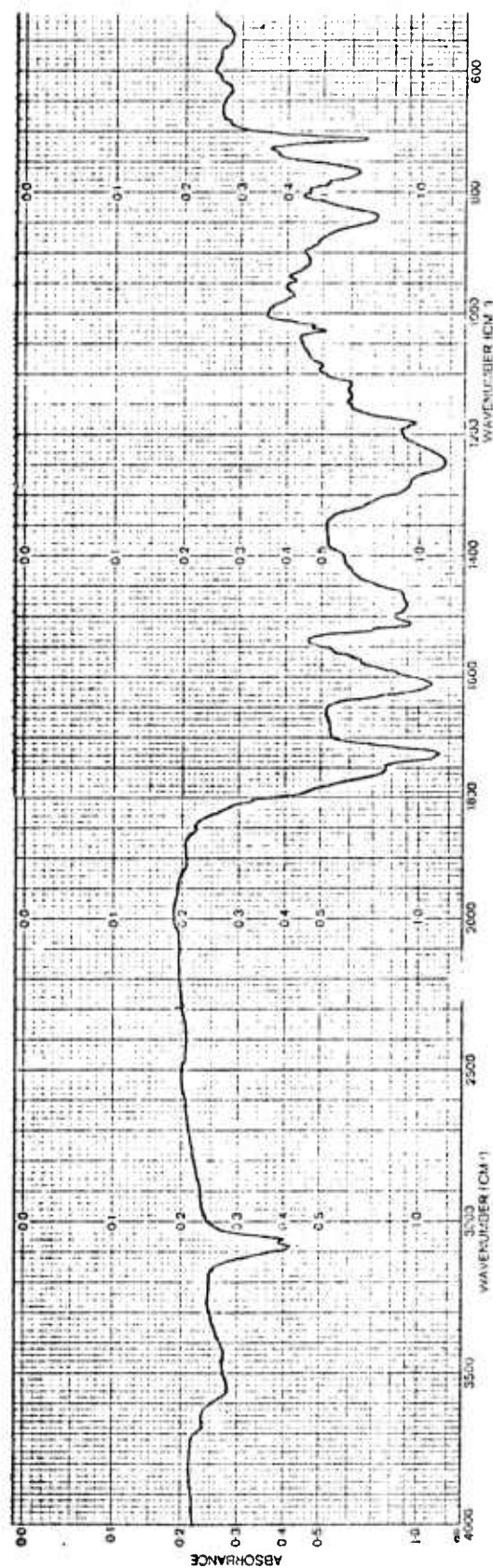


Figure 9. Infrared Spectrum of Polymer 25 after heating in air at 265°C for 4 hr.



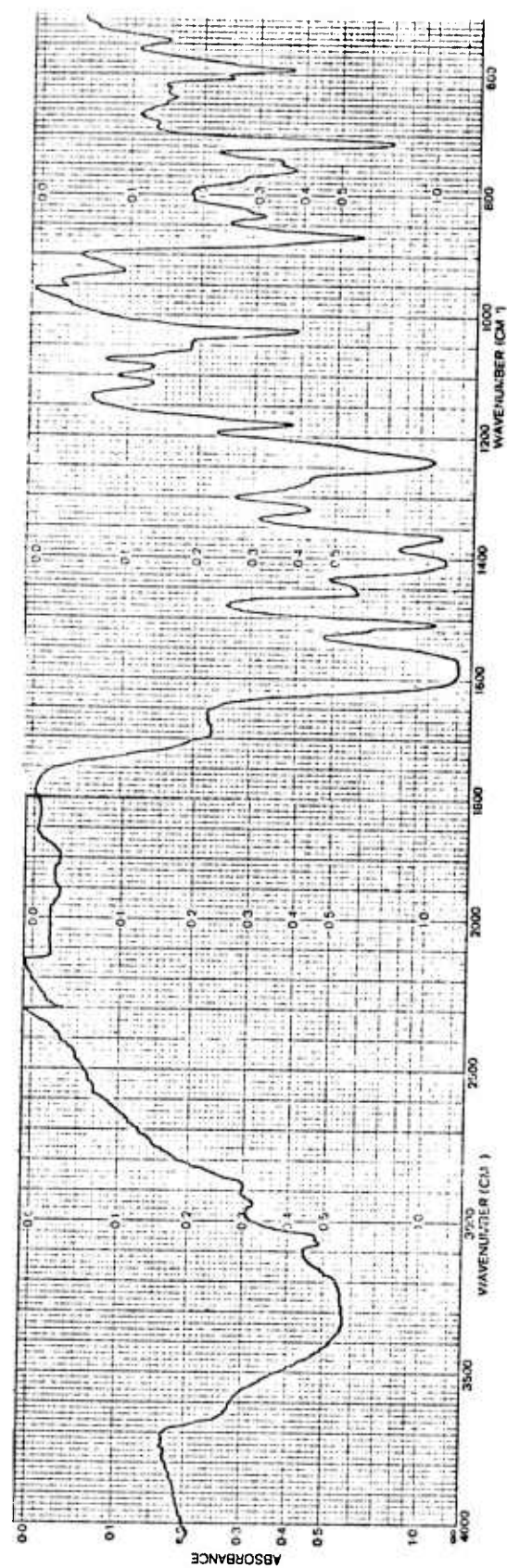


Figure 10. Infrared Spectrum of Polymer 26.



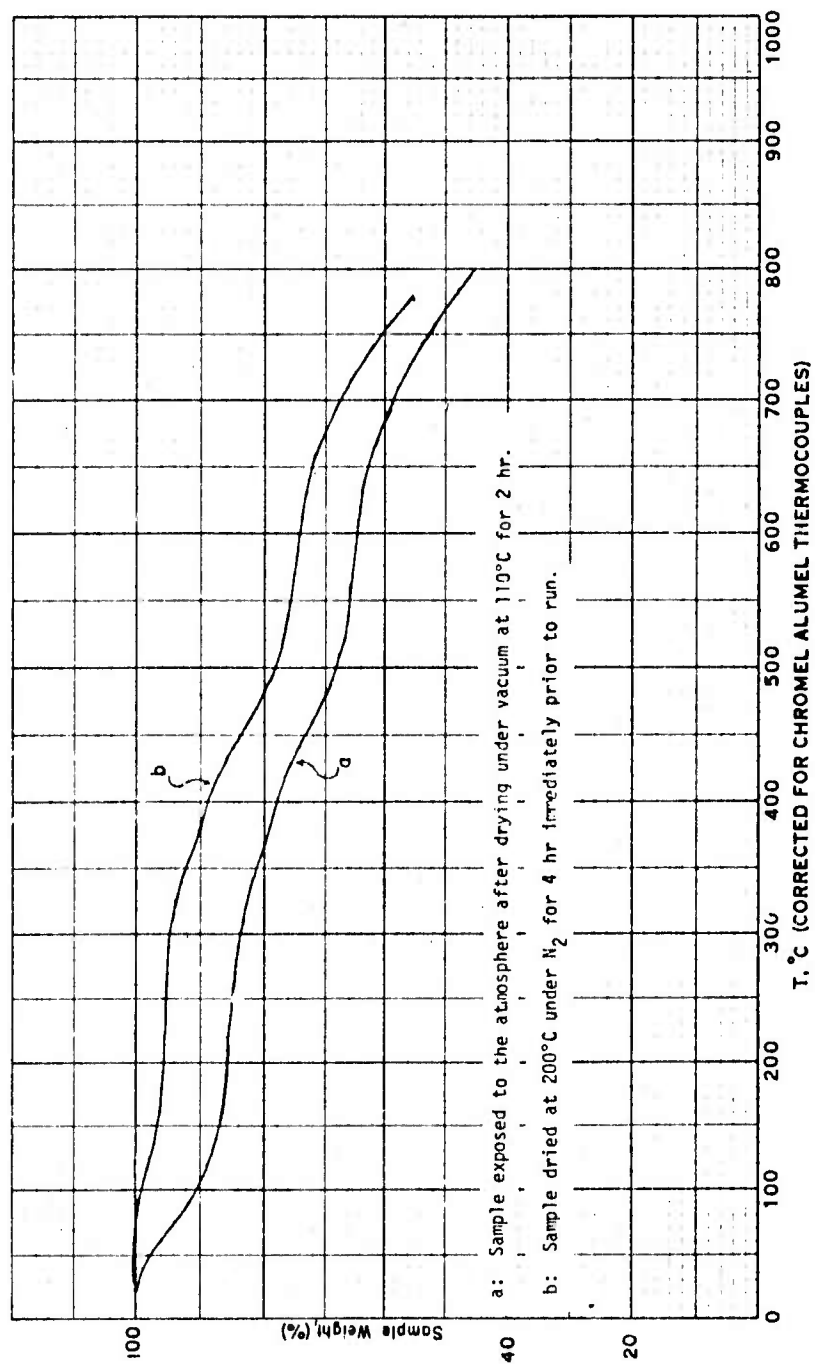


Figure 11. Thermogravimetric Analysis (N<sub>2</sub>) of Polymer 26.

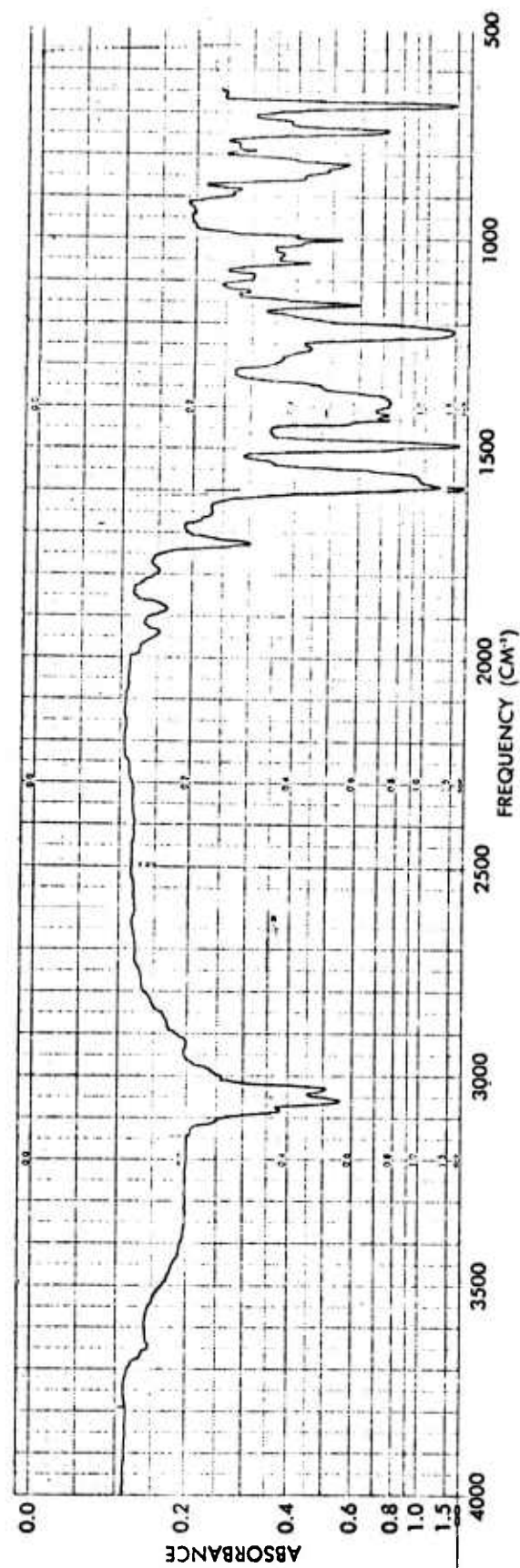


Figure 12. Infrared Spectra of Polymer 27a.

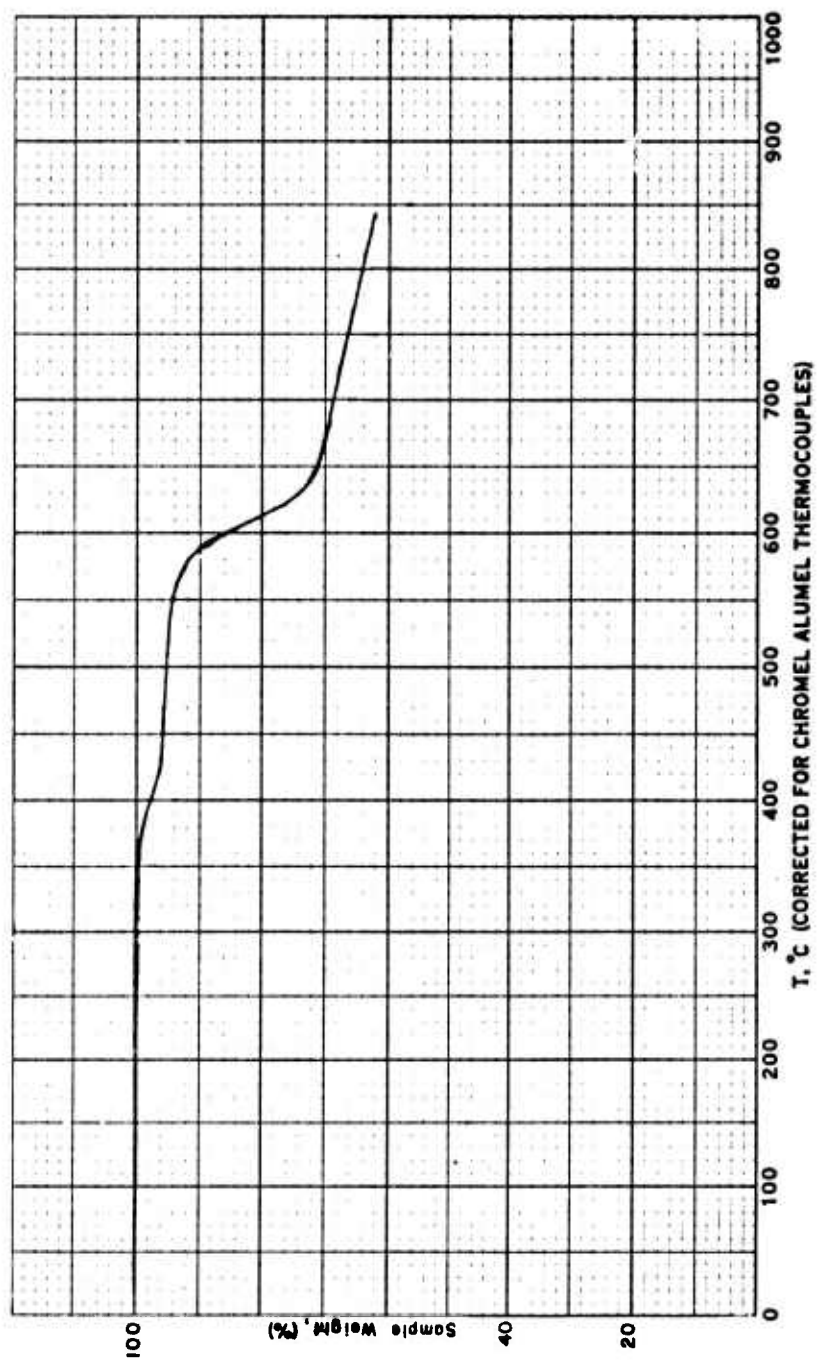


Figure 13. Thermogravimetric Analysis ( $N_2$ ) of Polymer 27a.

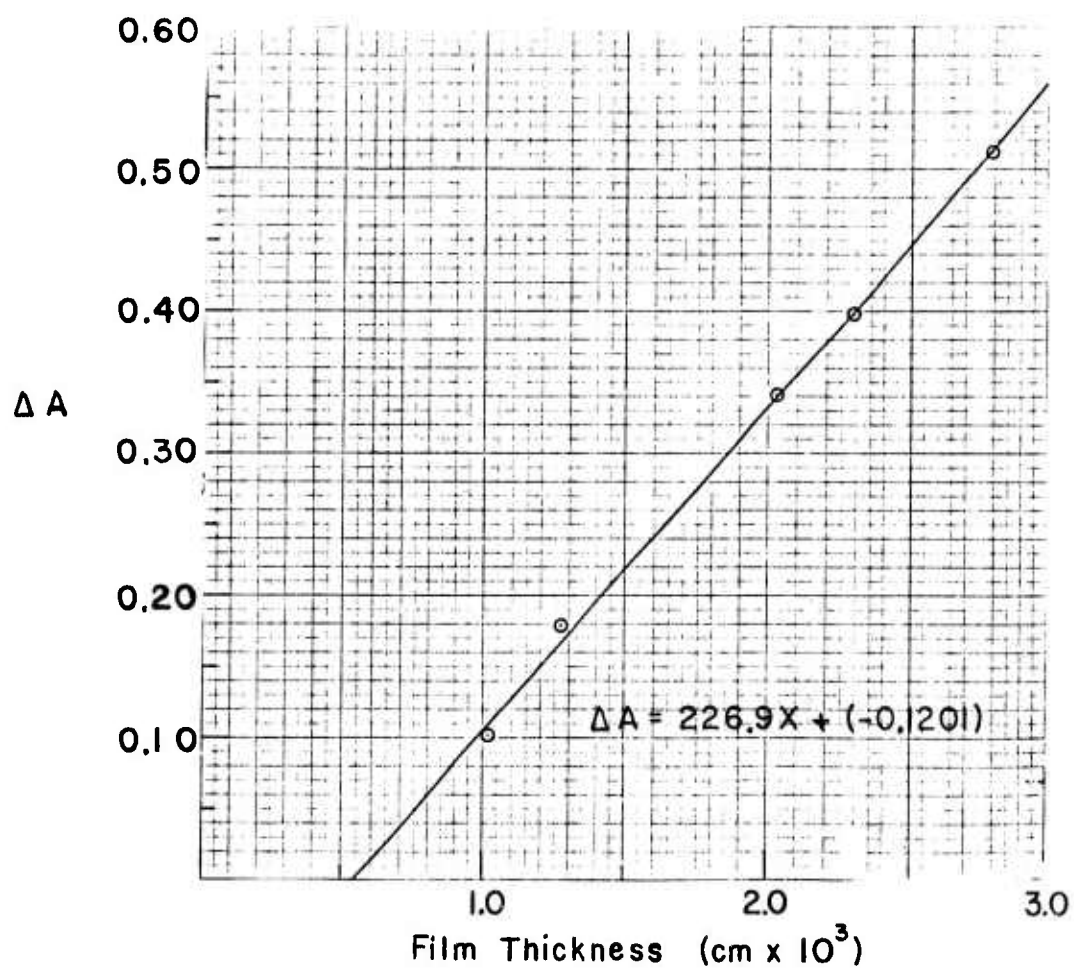


Figure 14. Plot of Film Thickness vs. Ester Carbonyl Absorption for Polymer 16a.

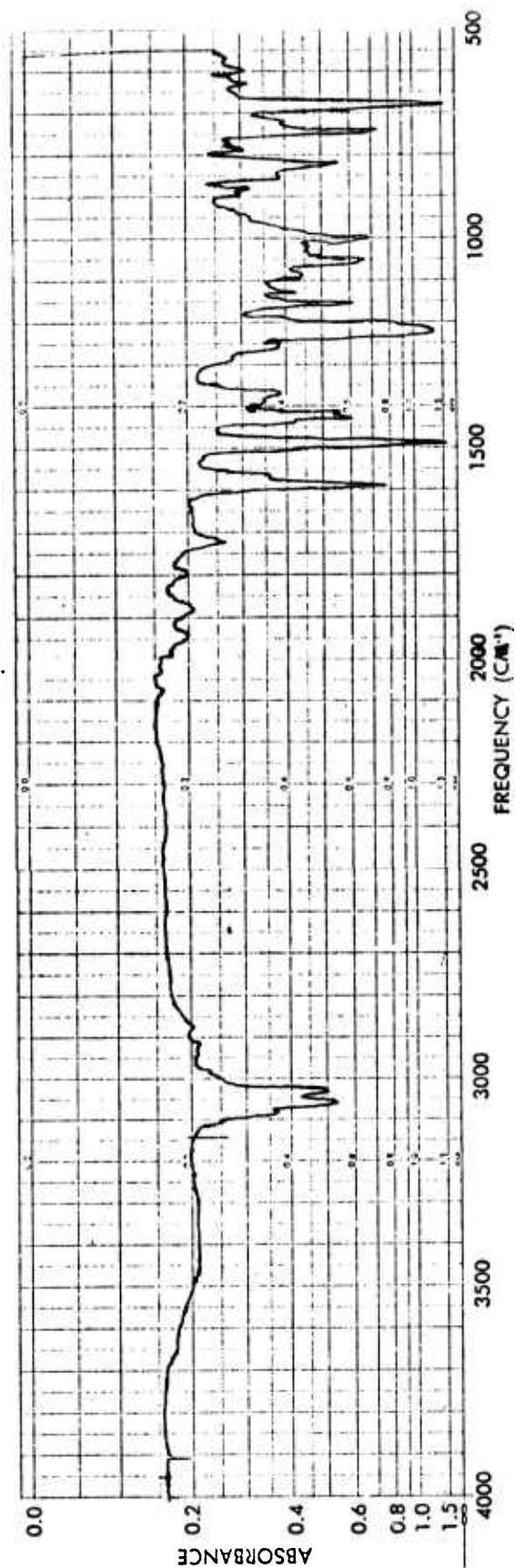


Figure 15. Infrared Spectra of Polymer 27d.

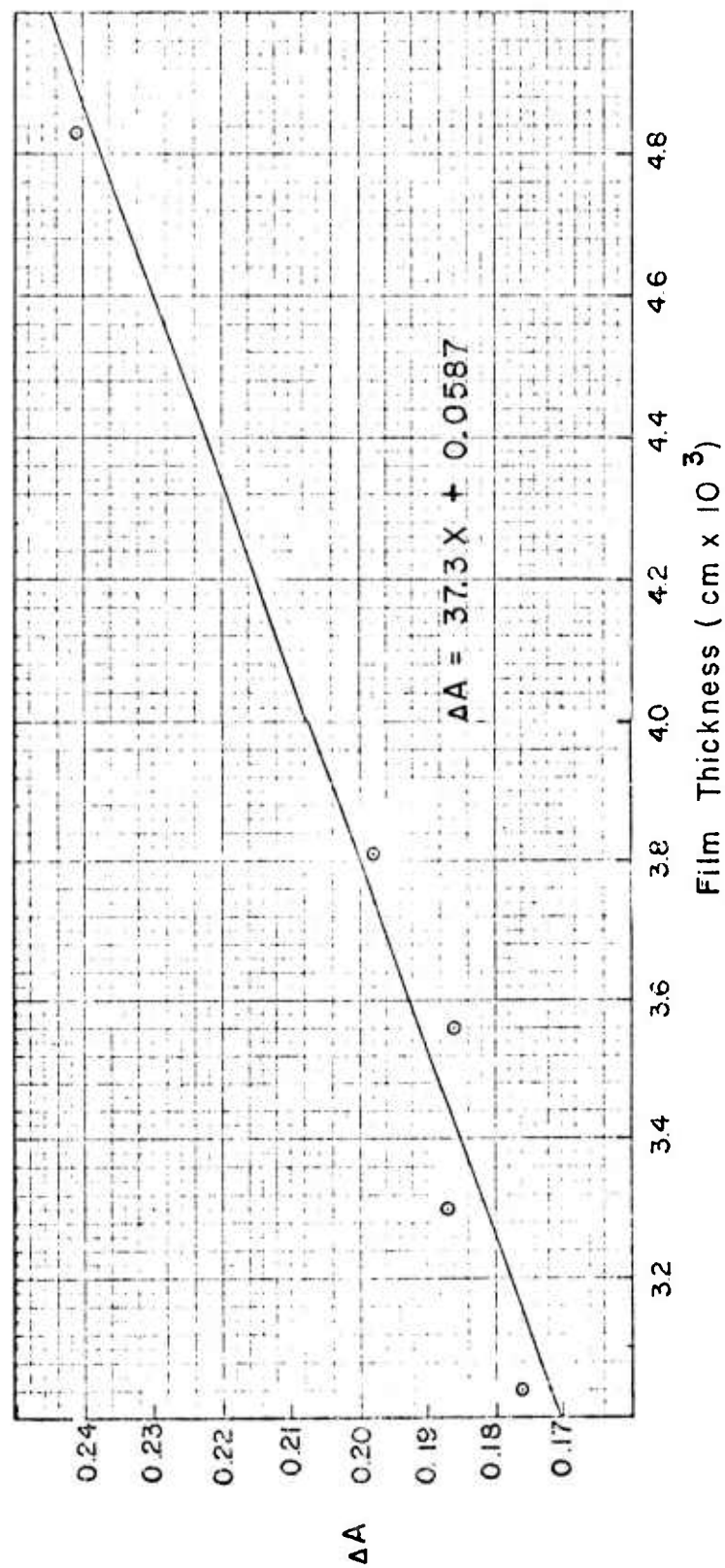


Figure 16. Plot of Film Thickness vs. Ester Carbonyl Absorption for Polymer 16b.



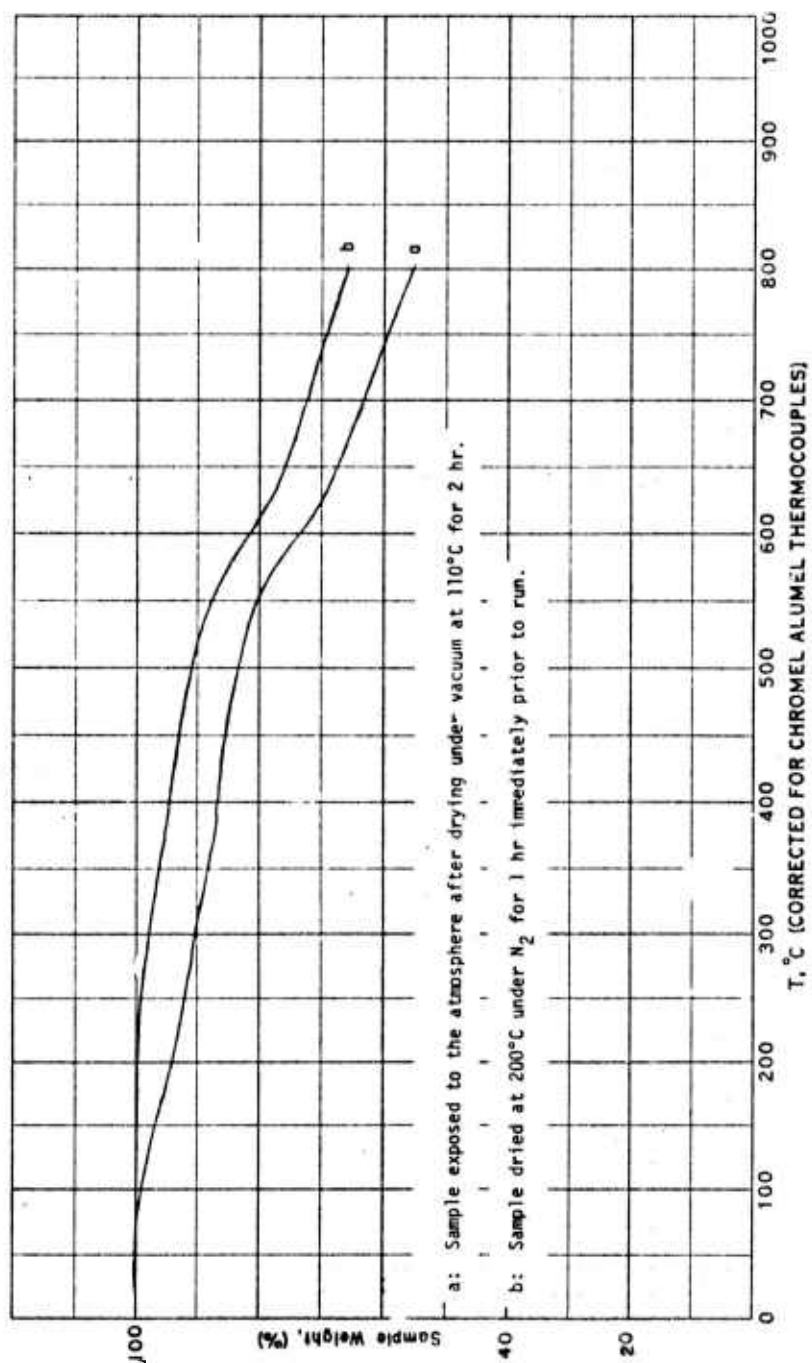


Figure 17. Thermogravimetric Analysis (N<sub>2</sub>) of Polymer 28.



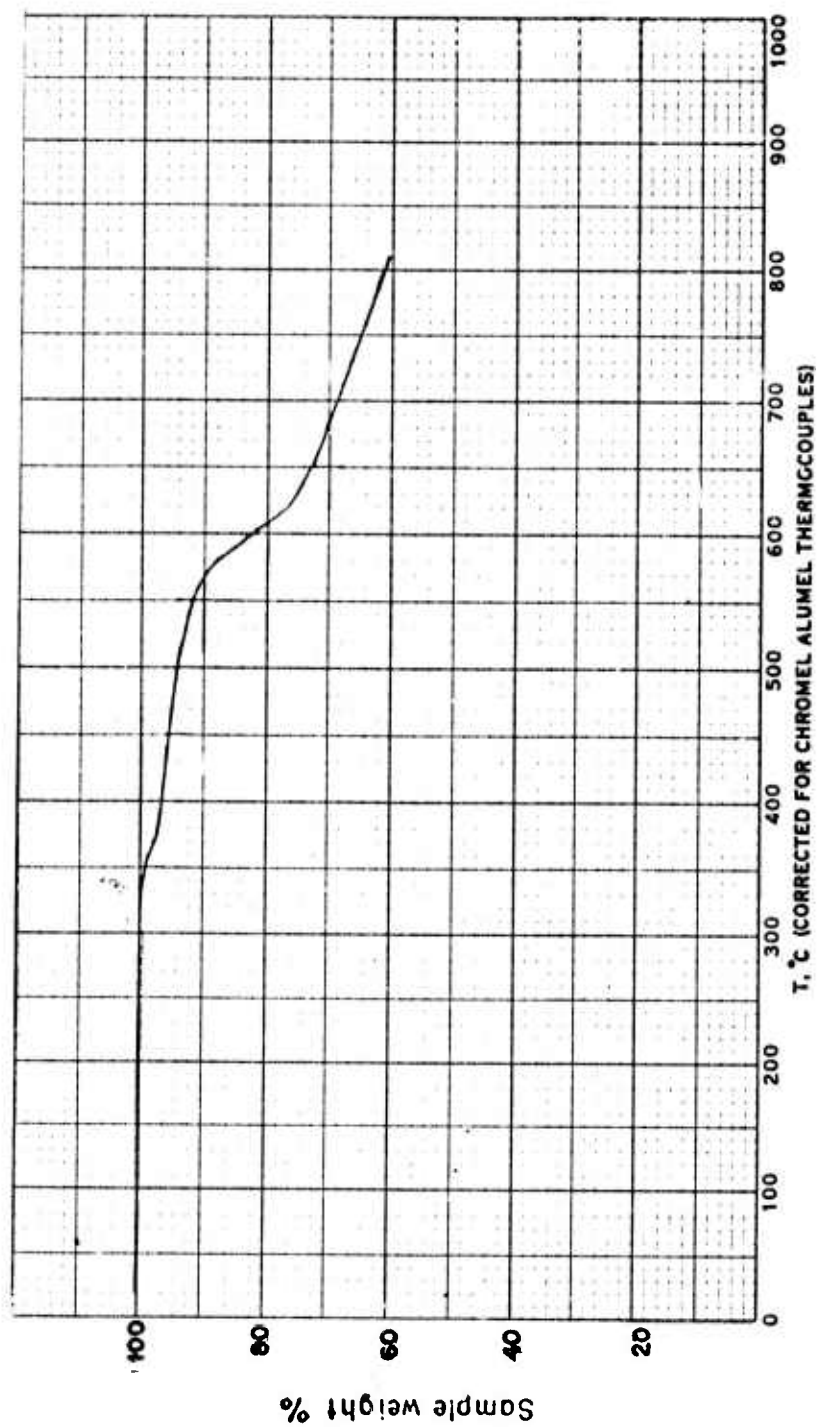


Figure 18. Thermogravimetric Analysis of Polymer 29.

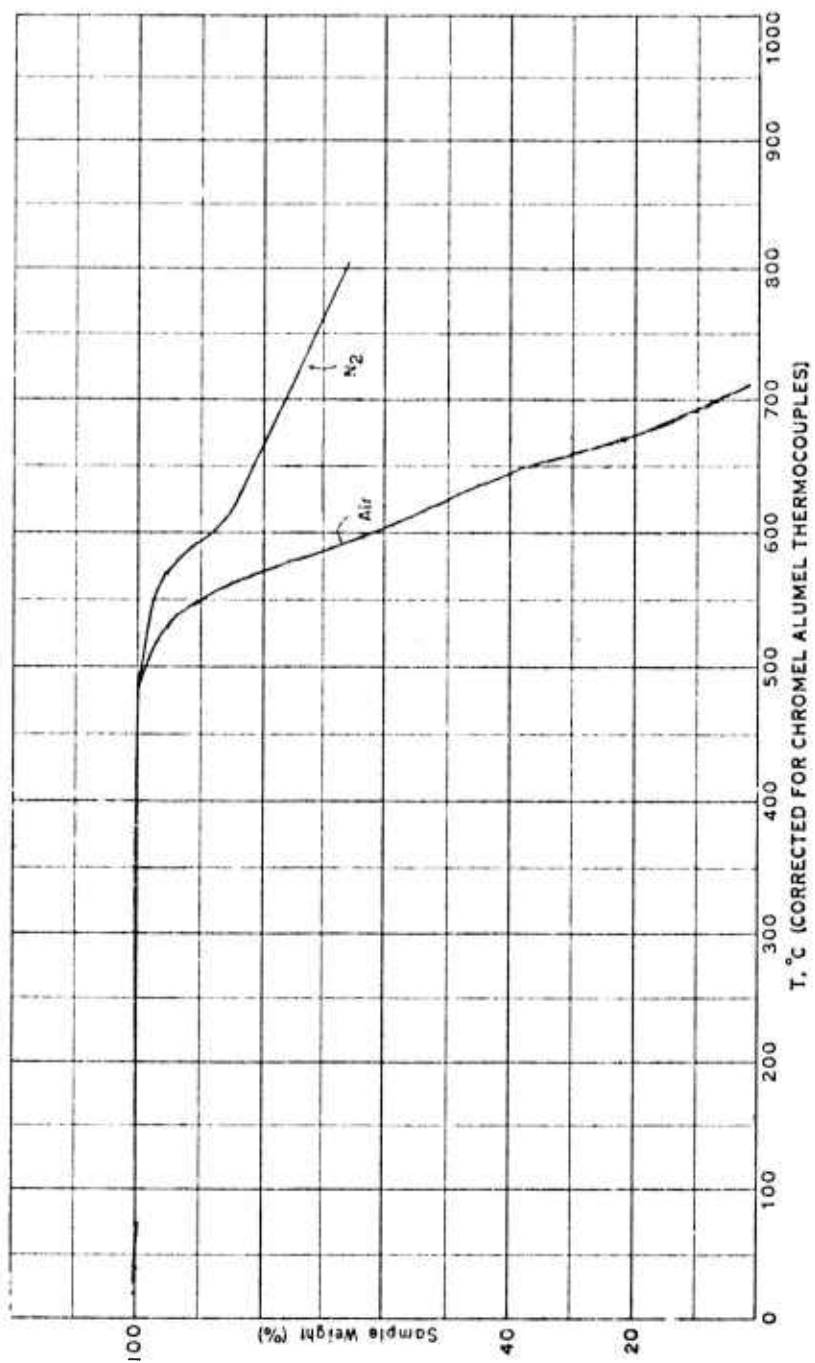


Figure 19. Thermogravimetric Analysis of Polymer 31.

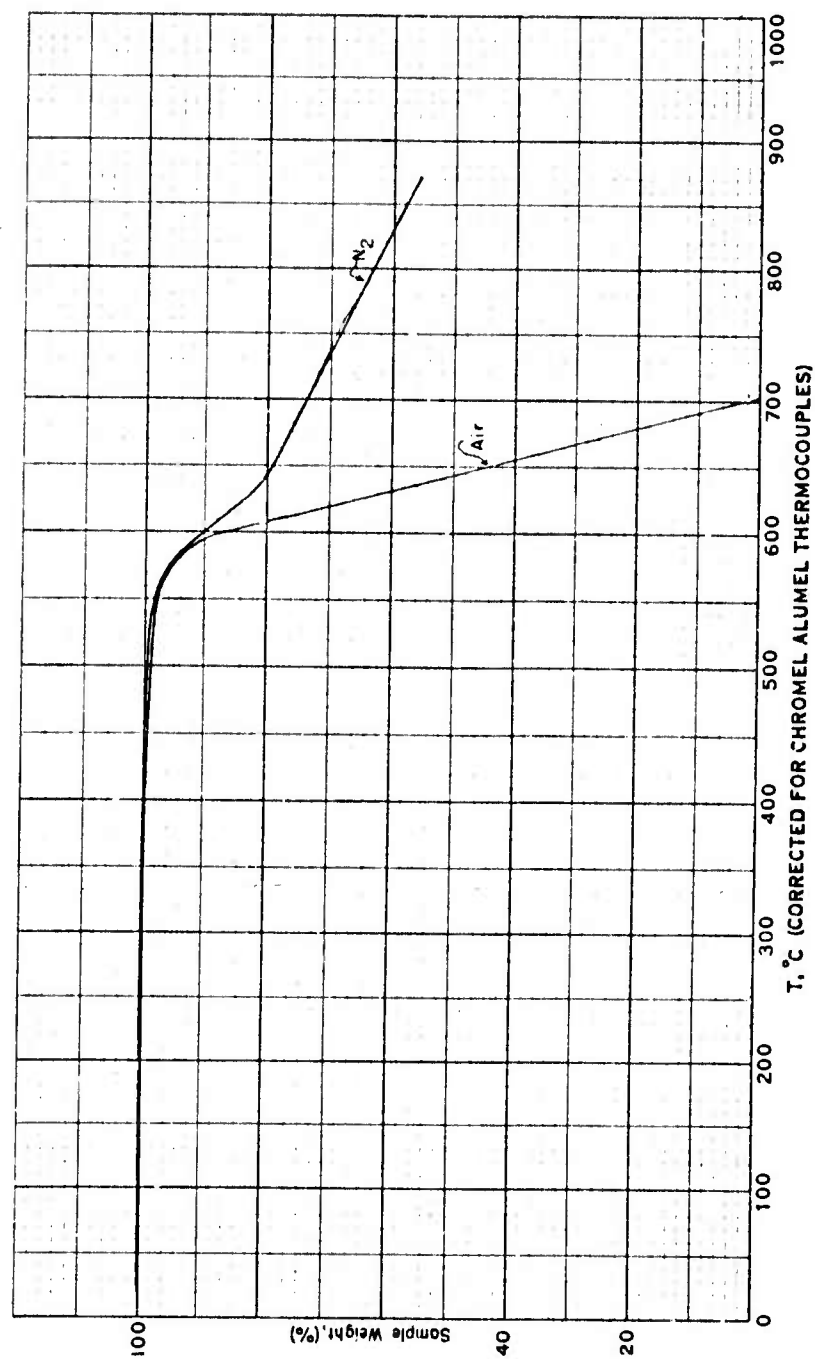


Figure 20. Thermogravimetric Analysis of Polymer 44.

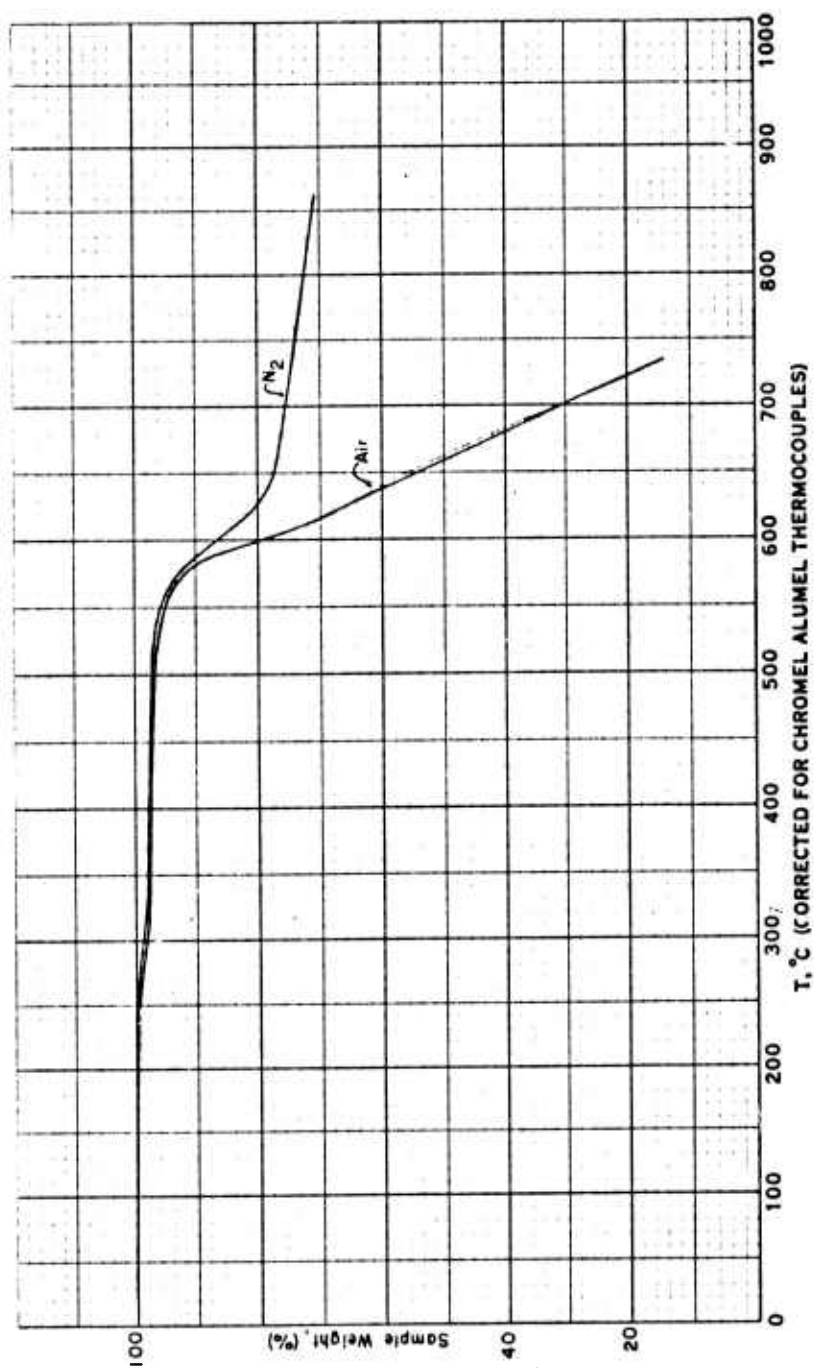


Figure 21. Thermogravimetric Analysis of Polymer 44 Hydrochloride.

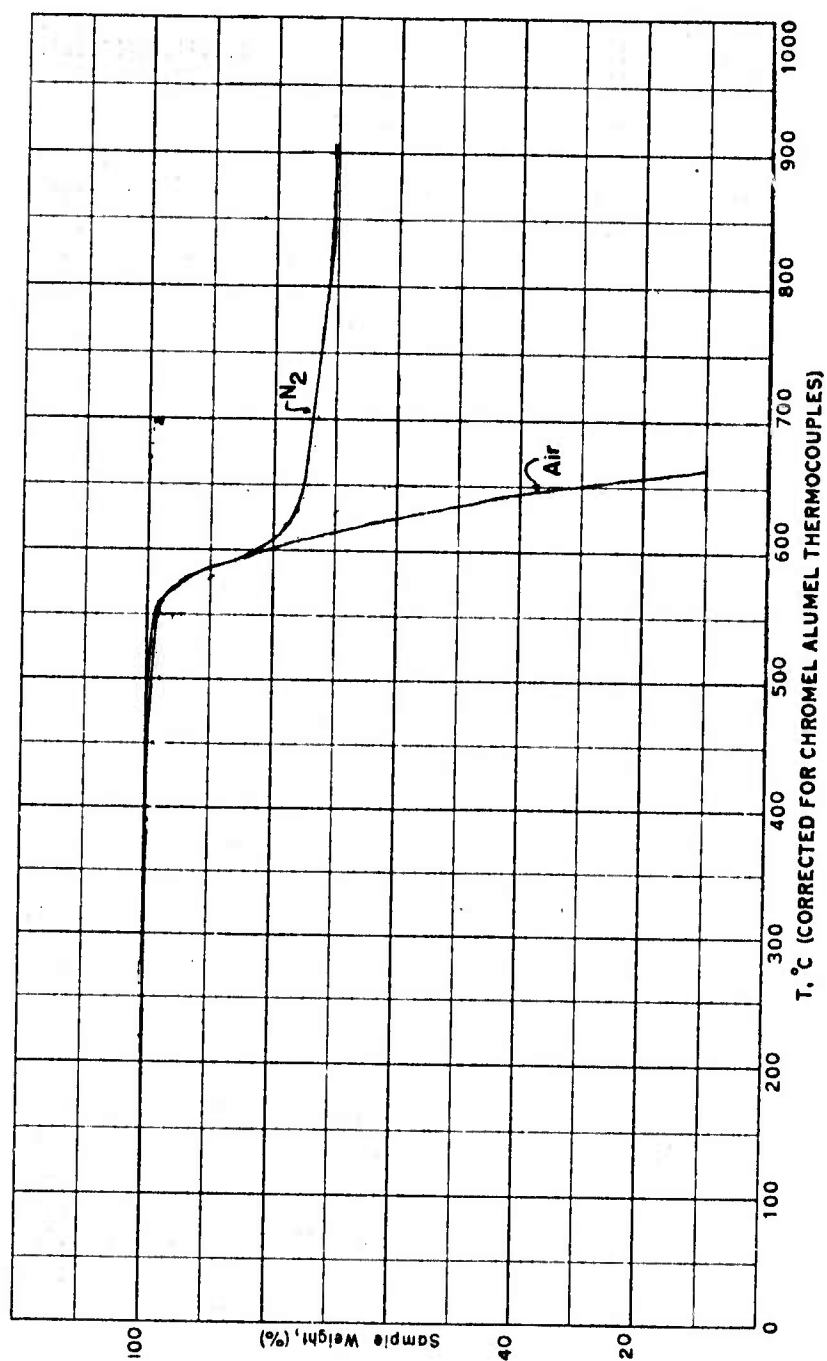


Figure 22. Thermogravimetric Analysis of Polymer 56a.

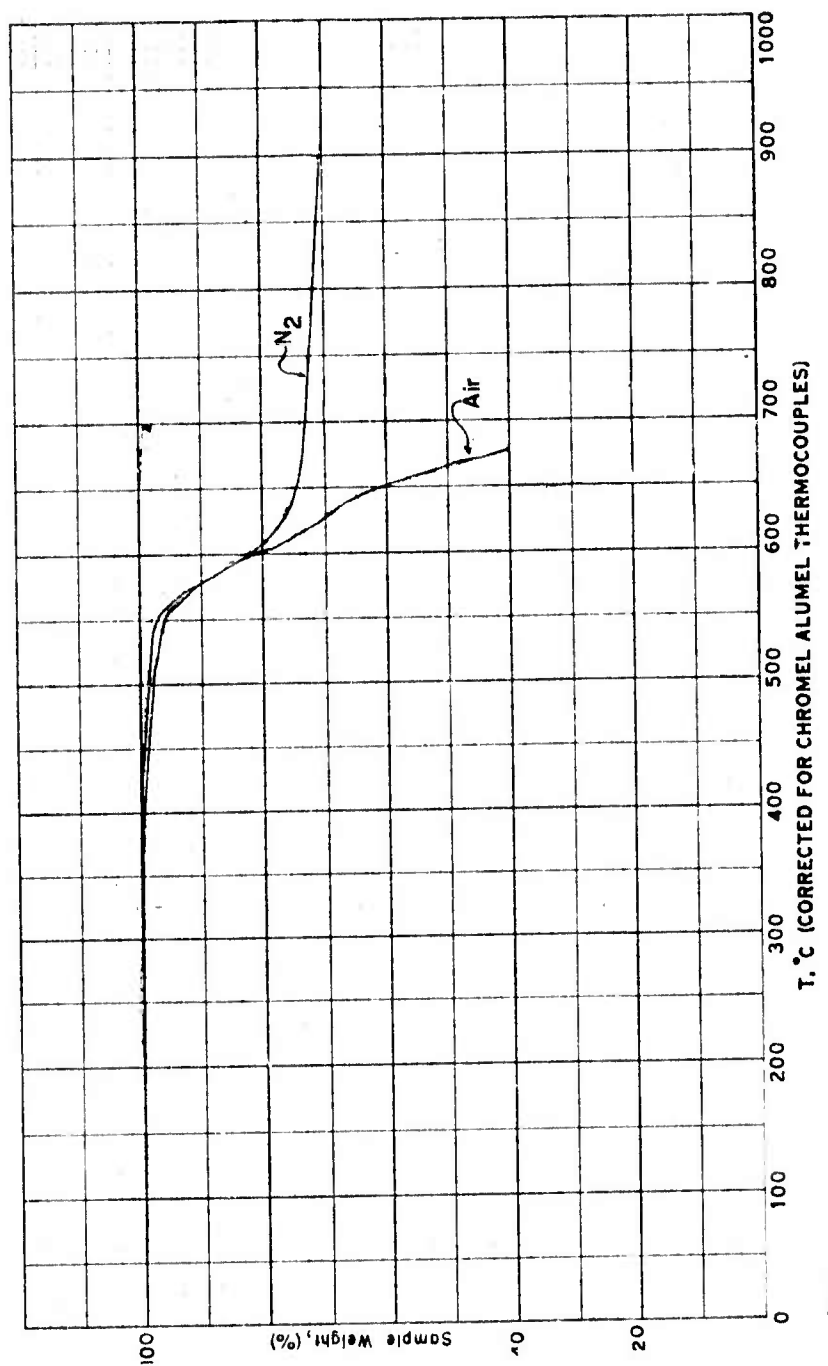


Figure 23. Thermogravimetric Analysis of Polymer 56b.

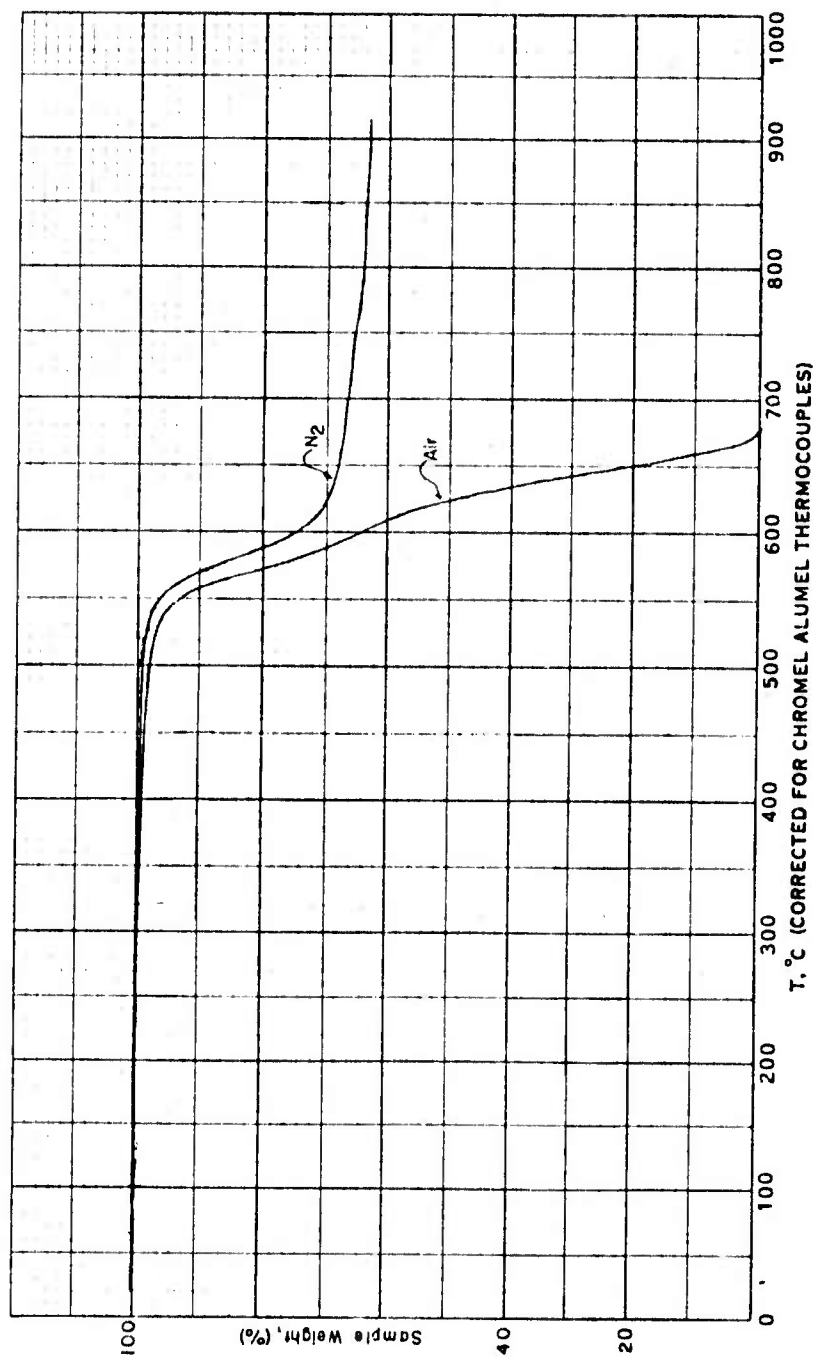


Figure 24. Thermogravimetric Analysis of Polymer 58.



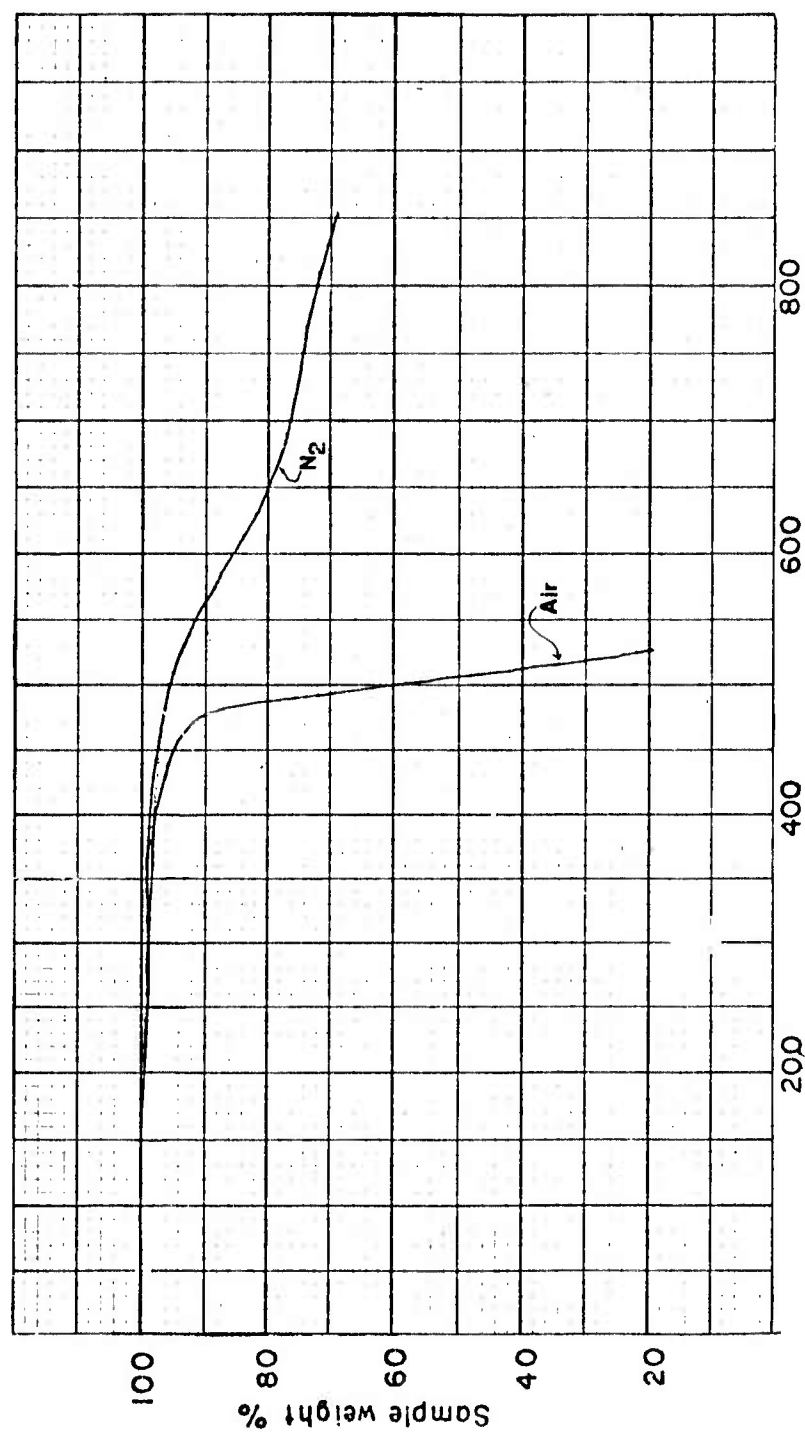


Figure 25. Thermogravimetric Analysis of Polymer 90.

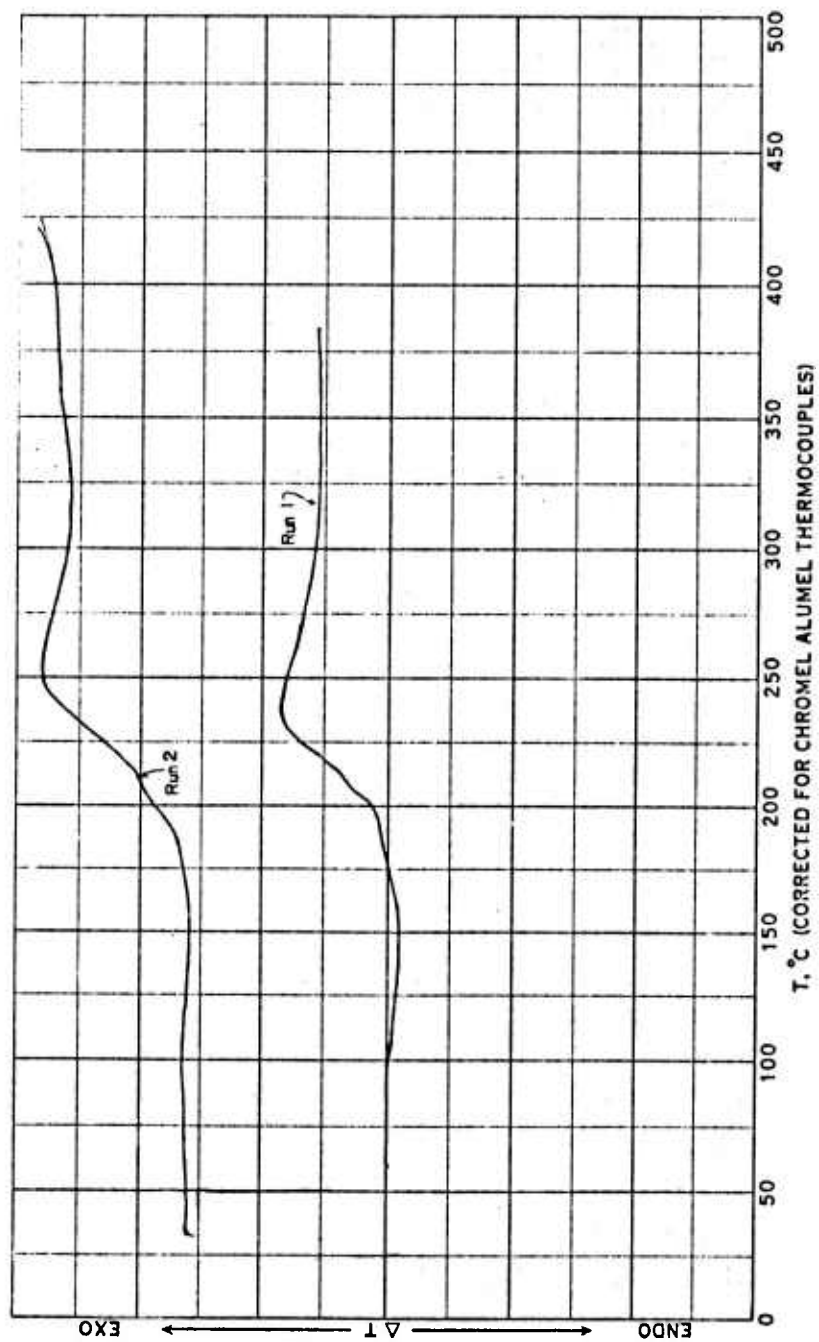


Figure 26. DSC Thermogram of Oligomers 91a-c.

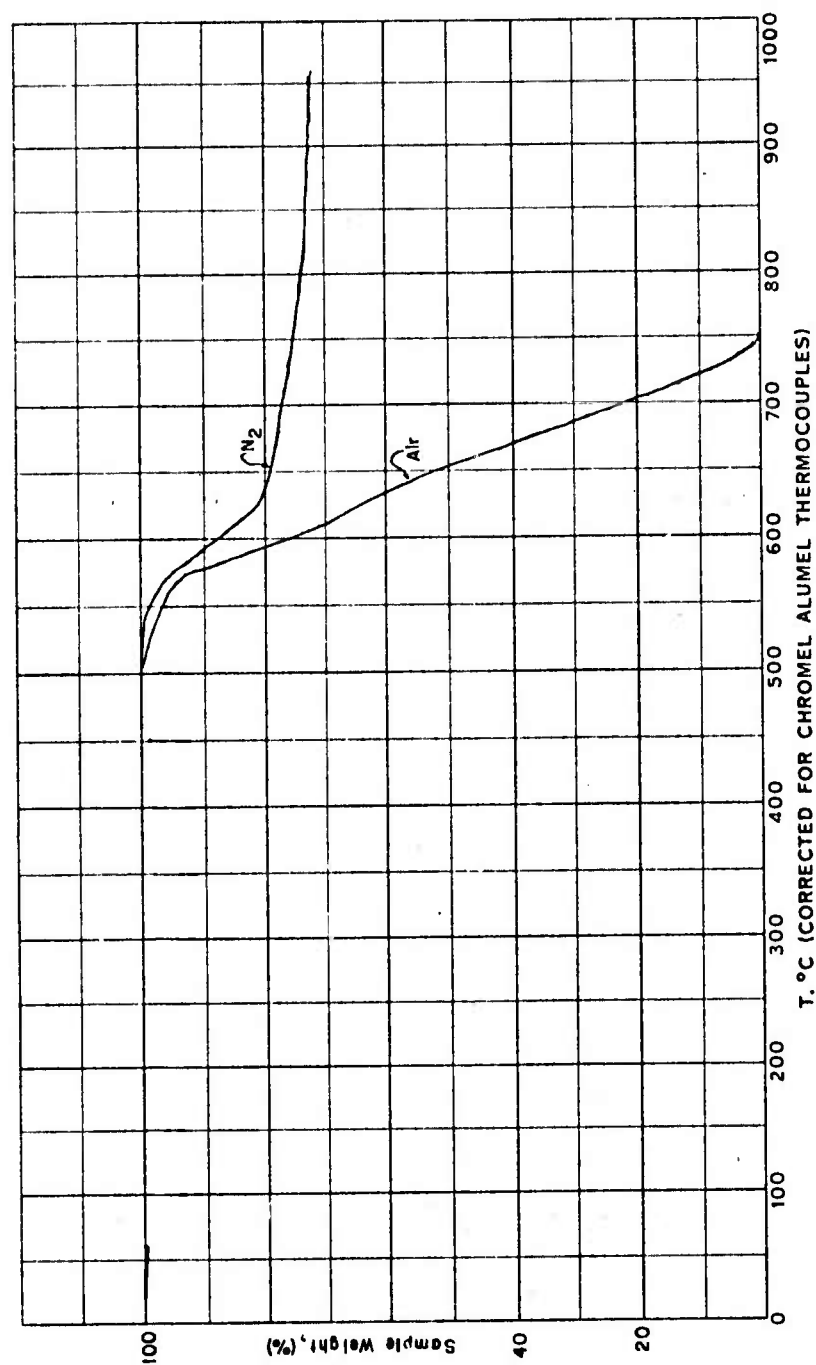


Figure 27. Thermogravimetric Analysis of Oligomers 91a-c.

## REFERENCES

1. B.A. Reinhardt, M.S. Thesis, Wright State University, Dayton, Ohio, 1974.
2. F.W. Harris, W.A. Feld, and L.H. Lanier, Am. Chem. Soc., Polymer Preprints, 16 (1), 520 (1975).
3. N.L. Zutty, J.A. Fancher, and S. Bonotto, "Encyclopedia of Polymer Science and Technology", Vol. 6, N.M. Bikales, ed., John Wiley and Sons, Inc., New York, 1967, p. 420.
4. A.H. Landrock, *ibid.*, Vol. 8, 1968, p. 782.
5. A.L. Landis, N. Bilow, R.H. Boschan, and R.E. Lawrence, Am. Chem. Soc., Polymer Preprints, 15 (2), 537 (1974).
6. R.F. Kovar, G.F.L. Ehlers, and F.E. Arnold, Am. Chem. Soc., Polymer Preprints, 16 (2), 246 (1975).
7. H. Mukamal, F.W. Harris, and J.K. Stille, J. Polym. Sci., Part A-1, 5, 2721 (1967).
8. I.L. Kotlyarevskii, M.S. Shvartsberg, V.N. Andrievskii, and B.G. Krugler, Izv. Akad. Nauk., SSSR, Ser. Khim., 1963, 2032; CA 60, 9367 (1964).
9. K. Bodendorf, and R. Mayer, Chem. Ber., 98 (11), 3554 (1965); CA 64, 627 (1966).
10. A.M. Krubiner, N. Gottfried, and E.P. Oliveto, J. Org. Chem., 34, 3502 (1969).
11. C.F.H. Allen, Chem. Rev., 62, 653 (1962).
12. R.W. Rees and D.J. Vaughan, Am. Chem. Soc., Polymer Preprints, 6, 287 (1965).
13. F.C. Chang and N.F. Wood, Tetrahedron Letters, 2969 (1964).
14. R.M. Silverstein and G.C. Bassler, "Spectrophotometric Identification of Organic Compounds", 2nd Ed., John Wiley and Sons, New York, 1967.
15. C.J. Pederson, J. Am. Chem. Soc., 89, 7017 (1967).
16. J. Stanek and M. Honak, Collection Czech. Chem. Comm., 15, 1037 (1951); CA 46, 7100e (1952).
17. G. Schening and L. Winterhalder, Ann., 437, 126 (1929).
18. E. Eaborn, A.R. Thompson, and D.R.M. Walton, J. Chem. Soc., 1364 (1967).
19. W.J. Dale, L. Starr, and C.W. Strobel, J. Org. Chem., 26, 2225 (1961).
20. M. Suzuki and B. Shimizu, J. Pharm. Soc. Japan, 73, 392 (1953); CA 48, 3294i (1954).
21. J.M. Watson, Macromolecules, 5 (3), 331 (1972).

22. H. Degiorgi and S.V. Zappi, Bull. Soc. Chim., 4, (5), 1636 (1937); CA 32, 5192 (1938).
23. Bolamm, Acta Chem. Scand., 16, 767 (1962).
24. T.L. Fletcher, M.S. Namkong, W.H. Wetzel, and H.L. Pan, J. Org. Chem., 25, 1347 (1960).
25. H. Gee and J. Harley-Mason, J. Chem. Soc., 251 (1947).
26. P.M. Hergenrother and D.E. Kiyohara, Macromolecules, 3, 387 (1970).
27. C.M. Suter and F.O. Green, J. Am. Chem. Soc., 59, 2578 (1937).
28. Beilstein, 9<sup>2</sup>, 656.
29. F. Arnold, private communication.
30. S.G.P. Plant and C.R. Worthing, J. Chem. Soc., 1278 (1955).
31. A.L. Williams, R.E. Kinney, and R.F. Bridger, J. Org. Chem., 32, 2501 (1967).
32. J.M. LaLancette and J.R. Brindle, Can. J. Chem., 49, 2990 (1971).
33. C.T. Redemann and C. Ernst Redemann, "Organic Synthesis", Coll. Vol. 3, E.C. Horning, ed., John Wiley and Sons, Inc., New York, 1955, p. 69.
34. L.I. Smith and J.W. Opie, "Organic Synthesis", Coll. Vol. 3, E.C. Horning, ed., John Wiley and Sons, Inc., New York, 1955, p. 56.
35. W.E. Kuhn, "Organic Synthesis", Coll. Vol. 2, A.H. Blatt, ed., John Wiley and Sons, Inc., New York, 1943, p. 447.
36. von Paul Ruggli, and F. Lang, Helv. Chim. Acta, 21, 38 (1938).
37. J.F. Bunnett and R.M. Conner, "Organic Synthesis", Coll. Vol. 5, H.E. Baumgarten, ed., John Wiley and Sons, Inc., New York, 1973, p. 478.
38. P. Pfeiffer and E. Kramer, Chem Ber, 46, 3655 (1912).

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